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16. ABSTRACT
The report gives preliminary data on methodology for candidate principal organic hazardous constituents (POHCs) that represent a variety of compound types, including alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acids, aliphatic and aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics. This work (and that under Contract 68-02-3696, Task 1) involved the evaluation of generalized GC/FID, GC/MS, and HPLC/UV methods for determining approximately 170 compounds from the approximately 400 compounds in Appendix VIII, Part 261, 40 CFR. However, the survey-analysis portion of waste characterization often targets specific compounds for determination in incinerator effluent that are not amenable to previously developed methods. Therefore, current research involves the development of specific GC/FID, GC/MS, and HPLC/UV methods for the determination of several of these compounds. The EPA has proposed regulations for owners and operators of facilities that treat hazardous wastes by incineration to ensure that these incinerators will be operated in an environmentally responsible manner. The primary criterion upon which the operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator (= or > 99.99%).

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Volume 1, Part 1

by

Ruby H. James
Joe M. Finkel
H. Kenneth Dillon
Herbert C. Miller

SOUTHERN RESEARCH INSTITUTE
2000 Ninth Avenue South
P.O. Box 55305
Birmingham, AL 35255-5305

and

Afaf K. Wensky

BATTELLE-COLUMBUS LABORATORIES
505 King Street
Columbus, OH 43201

Contract 68-02-2685
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EPA Project Officer: Larry D. Johnson

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, NC 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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FOREWORD

This report has been prepared by Southern Research Institute as part of ongoing studies in support of regulatory programs of Environmental Protection Agency's (EPA's) Air and Energy Engineering Research Laboratory, Research Triangle Park, North Carolina. This report contains criteria for the analysis methods for determination of principal organic hazardous constituents (POHCs) from the combustion of hazardous waste. The data in this report are intended as a reference to be used by laboratories that are monitoring the hazardous-waste streams of incineration facilities. Because of subtle differences among laboratories and analytical instrumentation, analysts who participate in similar studies should generate data that will establish their own criteria for the analysis of POHCs.

ABSTRACT

As part of the Resource Conservation and Recovery Act of 1976, the U.S. Environmental Protection Agency has proposed regulations for owners and operators of facilities that treat hazardous wastes by incineration to ensure that these incinerators will be operated in an environmentally responsible manner. The primary criterion upon which the operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. The DRE value, defined in terms of waste-input and stack-output levels of designated principal organic hazardous constituents (POHCs), must be equal to or greater than 99.99%.

In support of the DRE requirement, we evaluated and, when necessary, modified generalized GC/FID, GC/MS, and HPLC/UV analysis methods for the determination of approximately 70 candidate POHCs. These candidate POHCs represent a variety of compound types, including alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acids, aliphatic and aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics.

The developed generalized GC/MS and HPLC/UV methods are suitable for inclusion in the POHC Method Manual, Sampling and Analysis Methods for Hazardous Waste Combustion (EPA-600/8-84-002). The methods were applied to the determination of candidate organic compounds over concentration ranges of interest and demonstrated acceptable precision in the determination of most of the compounds.

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ABBREVIATIONS AND SYMBOLS

amu	Atomic Mass Unit
Appendix VIII	Hazardous Constituents List (Part 261, 40 CFR)
CFR	Code of Federal Regulations
DFTPP	Decafluorotriphenylphosphine
DNPH	Dinitrophenylhydrazine
DRE	Destruction and Removal Efficiency
EI	Electron Impact Ionization Mode
EPA	U.S. Environmental Protection Agency
g	Gram
GC	Gas Chromatography
GC/FID	Gas Chromatography/Flame-Ionization Detection
GC/MS	Gas Chromatography/Mass Spectrometry
h	Hour
HI	Hydroiodic Acid
HPLC	High-Performance Liquid Chromatography
HPLC/UV	High-Performance Liquid Chromatography/ Ultraviolet Spectrometry Detection
ID	Internal Diameter
is	Internal Standard
μg	Microgram (10^{-6} g)
μL	Microliter (10^{-6} L)
mg	Milligram (10^{-3} g)
mL	Milliliter (10^{-3} L)
mm	Millimeter (10^{-3} m)
MM5	Modified Method 5 Sampling Train
mol wt	Molecular Weight
ms	Millisecond
m/z	Mass to Charge Ratio
ng	Nanogram (10^{-9} g)
nm	Nanometer (10^{-9} m)
PAHs	Polynuclear Aromatic Hydrocarbons
POHCs	Principal Organic Hazardous Constituents
PICs	Products of Incomplete Combustion
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RRF	Relative Response Factor
RSD	Relative Standard Deviation
SASS	Source Assessment Sampling System
SIM	Selected-Ion Monitoring
s	Second
SD	Standard Deviation
SoRI	Southern Research Institute
TCDD	Tetrachlorodibenzo-*p*-dioxin
t_r	Retention Time
UV	Ultraviolet Spectroscopy
VOST	Volatile Organic Sampling Train

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SECTION 1

INTRODUCTION

REGULATORY REQUIREMENTS FOR THE INCINERATION OF HAZARDOUS WASTES

As part of the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency (EPA) has promulgated proposed, interim, and final regulations for the owners and operators of facilities that treat hazardous wastes by incineration. The purpose of the regulations is to ensure that such incinerators are operated in an environmentally responsible manner. The regulations cover a range of activities, including operational performance standards, waste analysis, trial burns, monitoring and inspections, recordkeeping and reporting, and the establishment of emission-control criteria (1). The specific details for each incinerator facility are authorized by facility permits.

The primary criterion upon which all operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. This value, which is defined in terms of waste-input levels and stack-output levels of the potentially hazardous substances, must be greater than 99.99% for proper incineration. The substances from the list in Appendix VIII, Part 261, 40 CFR have been designated principal organic hazardous constituents (POHCs), although many inorganic substances have also been included.

SAMPLING AND ANALYTICAL METHODS FOR HAZARDOUS-WASTE INCINERATION

As part of the supporting documentation for the permit writer and for the incinerator facility's owners and operators, the EPA has compiled a manual of methods for sampling and analysis for use in measuring the levels of POHCs in the various streams of an incinerator facility, including inlet wastes, stack gas, process waters, fly ash, and bottom ash (2). This manual is entitled "Sampling and Analysis Methods for Hazardous Waste Combustion" and shall be referred to as the Methods Manual hereafter. This manual expands upon and augments the information in the "Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incineration Units" (3).

This Methods Manual is intended to be a resource document for the preparation and execution of a sampling-and-analysis plan for hazardous-waste incinerators. The specific procedures described are primarily in the form of brief descriptions with reference to other documents that contain highly detailed description methods. Existing collections of sampling and analysis methods documentation such as "Test Methods for Evaluating Solid Waste" (SW-846) or "Samplers and Sampling Procedures for Hazardous Waste Streams" (EPA-600/2-80-018) have not been directly incorporated into the manual but are incorporated by reference (4,5).

During trial burns at an incineration facility, the sampling and analysis methods will allow measurement of those POHCs expected to be present in the waste and products of incomplete combustion (PICs). Also during trial burns, the waste samples may be characterized with the methods to establish limits on the waste composition that may be incinerated. During routine facility operation, the incoming wastes will be analyzed periodically to ascertain whether the composition of the waste has changed. Some gaseous species such as carbon monoxide will be monitored continuously, as specified in the Methods Manual, as an indicator of the combustion efficiency of the process. Periodically, at the frequency not specified in the current regulations, the influent and effluent streams are to be tested to monitor compliance with the DRE criteria.

Although the Methods Manual includes test procedures for proximate, survey, and directed (or specific-compound) analysis, our brief discussion here is limited to directed analysis because the modification of analytical methods applicable to the identification and quantification of POHCs is currently of primary interest to us (see Sections 4 and 5).

The directed-analysis portion of the waste-characterization scheme provides qualitative confirmation of compound identity and quantitative data with appropriate quality control for the potentially hazardous constituents that might reasonably be expected to be present in the waste, based on engineering judgment and on the results of proximate and survey analysis. Directed analysis does not involve screening every waste sample against the complete hazardous component list. A preliminary judgment is made as to the compounds or types of compounds that are likely to be present. The directed analysis then consists of the minimum set of analytical techniques that can be applied to the waste for qualitative identification and quantitative determination of the components that are actually present.

In practice, the results of the directed analysis will establish whether the waste contains the suspected pollutant and will demonstrate the concentration range at which the pollutant may be expected to be found. Directed analysis will also be used to confirm and quantify unexpected hazardous components identified in the survey analysis. These data on quantitative analysis of confirmed, identified contaminants of documented toxicity are essential for selection of appropriate POHCs to be monitored for the prediction of hazardous combustion by-products.

MODIFICATION OF DIRECTED-ANALYSIS METHODS

The Methods Manual recommends a variety of analytical techniques for the determination of the list of POHCs given in Appendix VIII, Part 261, 40 CFR. Whenever documentation was available to support the practice, the methods for the determination of organic compounds were written to incorporate a high-resolution analytical technique--fused-silica capillary gas chromatography--and a highly specific detection technique--mass spectrometry. Also, whenever possible, high-performance liquid chromatography (HPLC) was recommended for the determination of organic compounds that could not be determined by gas chromatography with mass spectrometric detection (GC/MS). Many compounds are amenable to analysis by either procedure. The application of these two approaches to the determination of as many of the POHCs as possible was designed to provide satisfactory qualitative analyses on a cost-effective basis for a variety of waste types and process chemistries.

For some of the compounds on the Appendix VIII list, there were limited references that recommended either GC/MS or HPLC analyses. For some compounds, the only analytical methods readily available were colorimetric or thin-layer chromatographic techniques. Other compounds required chemical derivatization to produce a product suitable for chromatographic analysis. For yet other compounds, no acceptable analytical method was found for inclusion in the Methods Manual. Furthermore, GC/MS or HPLC methods were documented for some compounds for which the operating conditions given for analysis were peculiar to the compounds and not readily adaptable to the determination needed to reduce the number or complexity of analytical methods in the Methods Manual, generalized GC/MS and HPLC techniques were developed for the determination of as many of the chemicals on the list of hazardous wastes as possible. Our effort was concentrated on a select number of POHCs (approximately 70) which are discussed later.

The subsequent sections of this report describe the efforts by Southern Research Institute to evaluate and, when necessary, modify GC/MS and HPLC/UV generalized analysis procedures for POHCs. This work is presented in Sections 4 and 5.

Battelle-Columbus Laboratories in a joint effort with Southern Research Institute undertook specific tasks to supplement the development of generalized test procedures. Specific analysis methods for brucine and 2-fluoroacetamide were developed. These compounds were not determined by the generalized procedures. Potentially useful air-sampling, sample-preparation, and analysis procedures for various POHCs including aldehydes, acids, esters, alcohols, and thiols were recommended. Many of these compounds were not included in the evaluation of the developed analysis procedures. Existing preparative and analysis methods for the determination of metals in wastes and incinerator effluents were refined and supplemented. Because this material is now largely historical and has been superseded by approaches in the final revision of the Methods Manual, we included the information in the Appendix D of our report.

SECTION 2

CONCLUSIONS

Generalized GC/FID, GC/MS, and HPLC/UV methods were developed for the determination of approximately 70 POHCs. The candidate POHCs were a variety of compound types, including alcohols, esters, chlorinated aliphatic and aromatics, carboxylic acids, aliphatic aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics.

The developed generalized methods were suitable for inclusion in the POHC Methods Manual. The methods were applied to the determination of candidate organic compounds over concentration ranges of interest and have demonstrated acceptable precision in the determination of most of the compounds.

The ultimate utility of the methods in the determination of POHCs in incinerator wastes and effluent will of course depend on the prudent choice of appropriate sampling procedures and sample-preparation procedures. As part of our work, therefore, we have compiled proposed overall air-sampling, sample-preparation, and analysis procedures for a variety of POHCs. The evaluation of the accuracy and precision of these total sampling and analytical methods should be the emphasis of future investigation.

Also under this work assignment, other tasks have been performed.

- Specific GC analysis methods were developed for two compounds, brucine and 2-fluoroacetamide. These compounds could not be determined by the generalized GC method.

- Existing generalized digestion procedures and specific analysis procedures for the determination of metals in wastes and incinerator effluent were also revised. The generalized digestion procedures were found suitable for the determination of three metals, beryllium, strontium, and vanadium, for which the procedure had not been evaluated previously.

SECTION 3

RECOMMENDATIONS

Several recommendations for future investigations are as follows:

- SoRI will continue to apply the general survey methods to those POHCs not yet evaluated.
- Based on SoRI's findings, the proposed screening program should be evaluated with incinerator-effluent samples, extracts, and sorbent media.
- In those cases where a generalized method was not sufficient to quantify a POHC, then more specific analytical techniques should be developed and evaluated on a priority basis.

SECTION 4

TECHNICAL APPROACH IN THE DEVELOPMENT OF GENERALIZED ANALYSIS METHODS

GENERAL CONSIDERATIONS

The primary focus of our experimental work was to develop two generalized analytical methods for the determination of POHCs in appropriate organic solvents. One analytical technique involved GC/MS with the use of a capillary column, and the other involved HPLC with ultraviolet/visible spectrophotometric detection (HPLC/UV).* During the optimization of the GC methods, flame-ionization detection (FID)--in addition to MS--was employed to aid in establishing operating conditions. The HPLC method was developed for use with reversed-phase C_{18} columns primarily because reversed-phase columns are less apt than normal-phase columns to adsorb organic analytes irreversibly. HPLC detection systems, other than ultraviolet/visible (UV/VIS) detection, were not considered because UV/VIS detection was judged to be more suitable for the development of a generalized HPLC test method. Because the UV/VIS detector can measure absorbances at selected wavelengths over a fairly broad range (190 to 600 nm), the detector offers selectivity and versatility in determining a variety of compound types.

The laboratory work was structured to lead systematically to the determination of the feasibility of developing generalized test methods. The resulting methods were applied to the determination of selected POHCs. First, we selected a variety of POHCs for preliminary investigation and performed analyses of standard solutions of mixtures of these POHCs (in appropriate solvents) to optimize instrumental operating conditions. Once suitable operating conditions had been established, an individual chromatogram for each of these POHCs was generated. Finally, we analyzed a series of standard solutions of each of the selected POHCs to estimate detection limits and to establish calibration curves. Also, multiple determinations were made on specific concentrations of selected POHCs to define the precision of the test methods.

SELECTION OF CANDIDATE POHCs

Several criteria were used in compiling the list of organic POHCs to be included in our investigations. First, some of the organic compounds listed in Appendix VIII, Part 261, 40 CFR, were eliminated from consideration in the method-development work. We excluded over 70 priority pollutants in the list because generalized analytical methods were available for their determination.

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*Although the detector is capable of measuring absorbances in both the ultraviolet and visible regions (190 to 600 nm), we use the acronym HPLC/UV, which is conventional for describing HPLCs with variable-wavelength detectors.

Several extremely hazardous compounds--including aflatoxins, cyanogen bromide, diisopropylfluorophosphate, mustard gas, and others--were not investigated for the following reasons: First, special handling procedures would likely have to be incorporated into methods for the determination of these compounds to eliminate the possibility of the analyst's being exposed to them. Second, the lability of some of the compounds would necessitate their transformation to stable analytes, a complication that would preclude the application of a straightforward GC/MS or HPLC/UV analytical procedure. Other compounds such as formaldehyde and other volatile aldehydes were not considered because derivatization schemes would be required to determine these compounds by GC/MS or HPLC/UV methods. Other less reactive volatile compounds including acetonitrile, bromoacetone, carbon disulfide, 1,2-dibromoethane, methyl ethyl ketone, and others were not investigated because their determination along with many of the less volatile compounds was impractical and because many can likely be determined by the EPA's generalized analytical method for volatile organic compounds.

From the remaining POHCs on the hazardous-compound list, we selected about 70 candidate compounds, largely on the basis of commercial availability. Included in this selection were a variety of compound types including alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acids and acid anhydrides, aliphatic and aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics. The candidate compounds were chosen from such a wide variety in an attempt to represent most of the compound types of the organic POHCs in the hazardous-compound list (i.e., Appendix VIII, Part 261, 40 CFR). The specific compounds selected are presented in Section 5 along with the analytical results.

Once we had selected the candidate POHCs, we divided the compounds into two primary groups--one groups for GC/MS investigations, the other for HPLC/UV studies. In general, thermally stable compounds that were expected to be vaporized at temperatures typical of gas-chromatographic operating conditions were selected for GC/MS work. Of course, compounds that were expected to be irreversibly adsorbed on GC columns were excluded from GC/MS work. We analyzed relatively nonvolatile compounds with molecular electronic absorption bands in the ultraviolet/visible wavelength ranged by HPLC/UV; these compounds included some materials such as saccharin and epinepherine for which the analytical methods recommended by the Methods Manual involved derivitization to produce products suitable for GC analysis. Other candidate POHCs that we investigated by HPLC/UV were compounds for which no chromatographic procedure was recommended in the Methods Manual, such as 5-nitro-*o*-toluidine and Trypan blue.

PREPARATION OF STOCK STANDARD SOLUTIONS

We prepared stock standard solutions of the candidate compounds in appropriate solvents at a concentration of either about 1 mg/mL or about 10 mg/mL. These stock solutions were serially diluted as required to prepare working standards.

We used primarily methylene chloride as the solvent in the preparation of standards for GC/MS studies. Several different polar solvents--acetonitrile, methanol, and water--were used in preparing solutions of POHCs determined by HPLC. A few candidate compounds required ionic solutions to effect dissolution. For instance, we dissolved epinephrine in dilute hydrochloric acid and melphalan in a 1:1 combination of 0.01 $\underline{M}$ NaH_2PO_4 and methanol.

GC ANALYSIS PROCEDURES

Description of Instruments and General Operating Conditions

We developed the GC/MS generalized test method on the Hewlett-Packard Model 5895 gas chromatograph/mass spectrometer-data system. The components of the instrument include a hyperbolic quadrapole mass filter with a convertible electron-impact (EI) and positive-ion chemical-ionization source, a capillary and jet separator GC/MS interface, and a data system that includes an HP2113 computer, a high-speed printer, a magnetic tape system, a 50-megabyte HP7920M disk-drive system, a communications interface, GC/MS operating software, and an unabridged NBS spectral library. The supplemental GC/FID work was performed on a Hewlett-Packard Model 5840 gas chromatograph that was equipped for use with capillary columns.

The work with both GC/MS and GC/FID involved capillary chromatography with matched, fused-silica SE-54 wallcoated capillary columns 25 m long, 0.31-mm ID. The initial operating conditions were chosen as a compromise of the conditions given for several capillary GC methods in the Methods Manual. The initial starting column temperature was 40 °C; the temperature was then programmed at 10 °C/min to 280 °C and maintained at 280 °C for 15 min. Injection and detection temperatures were 250 °C. The carrier gas was helium and was maintained at a volume flow rate through the column of about 2 mL/min. In the GC/FID work, the carrier-gas flow was split downstream from the injection port in the conventional manner at a ratio of about 1:40. Thus, only a small percentage of an injected sample was actually passed onto the column. In the GC/MS work, the "splitless" injection technique was employed. Consequently, we assumed that essentially all of the injected sample reached the column in GC/MS determinations.

Optimization of the GC/FID and GC/MS Procedure

GC operating conditions were optimized by analyzing solutions containing a variety of the candidate POHCs by the GC/FID technique. The column-head pressure was adjusted appropriately to maximize the FID response to test mixtures. We used these adjustments to pinpoint the optimum carrier-gas velocity, which in turn defined the splitting ratio.

Having established GC operating conditions by the GC/FID procedure, we then applied the method to the determination of the candidate POHCs by GC/MS. We also established reference mass spectra for the identification of the individual POHCs. The mass spectrometer was operated in a full-mass-scanning range (41 to 350 or 450 amu) in the EI mode. The scan time was maintained at ≤ 1 s to enable the collection of enough scans to characterize each capillary GC peak.

GC Quality-Control Procedures

We calibrated the GC/FID and GC/MS procedures with external standard solutions of the candidate POHCs. Five-point calibration curves were prepared for each candidate POHC determined by gas chromatography. Each curve was a plot of the FID or MS response (relative to anthracene-d_{10}) as a function of the quantity of the particular POHC injected on the GC column. The detection limit for each candidate POHC was estimated as the quantity (ng) of POHC on the GC column that gave rise to a signal approximately twice the background noise level. We also established reference mass spectra for the identification of the individual POHCs.

In addition to the use of external standards for the calibration of both GC/FID and GC/MS methods, other quality-control measures were implemented. The performance of the GC/MS system was checked daily with decafluorotriphenylphosphene (DFTPP) according to the requirements given in EPA Method No. 625 (6).

The precision of determinations by GC/FID and GC/MS was estimated by triplicate injections of at least one standard solution of each POHC investigated by gas chromatography. The estimate of precision of the replicate measurements is expressed as the relative standard deviation (RSD) calculated from Equation 1.

$$\text{RSD}\ (\%) = \left(\frac{\text{SD}}{X}\right) 100 \qquad (1)$$

Standard Deviation (SD) was calculated from Equation 2.

$$\text{SD} = \sqrt{\frac{\sum_{i=1}^{n} (X_1 - \overline{X})^2}{(n - 1)}} \qquad (2)$$

Mean relative response $(\overline{X})$ was calculated from Equation 3.

$$X = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad (3)$$

where

n = number of replicate measurements, and

X_i = relative response of the POHC standard.

Furthermore, we used anthracene-d_{10} as an internal standard in the GC methods. Along with the analytes we injected anthracene-d_{10} to minimize the effect of injection volume and instrument performance upon the precision of determinations. Also, the anthracene-d_{10} internal standard was used to calculate the relative response factor (RRF) for each POHC from Equation 4.

$$RRF = (A_s C_{is})/(A_{is} C_s) \qquad (4)$$

where

A_s = area of the characteristic ion for the POHC to be measured,

A_{is} = area of the characteristic ion for the internal standard,

C_{is} = concentration of the internal standard (µg/mL), and

C_s = concentration of the POHC (µg/mL) to be measured.

Recovery data were not applicable for this phase of the project because our analyses were done with neat solutions and standard mixtures of POHCs. We did not collect, prepare, or analyze field samples that required spiking of the matrix with surrogate standards or specific POHCs.

HPLC/UV ANALYSIS PROCEDURES

For the development of a generalized HPLC/UV analysis procedure, we used the Hewlett-Packard Model 1084B high-performance liquid chromatograph equipped with a variable-wavelength UV/VIS detector (190 to 600 nm) and an automatic sampling system. The following two reversed-phase columns were used with an acetonitrile/water eluent:

- Perkin-Elmer HC-ODS-SIL-X-1, 10-µm particle size, 25 cm long, 2.6-mm ID.
- Waters Associates µBondapak C_{18}, 10-µm particle size, 30 cm long, 3.9-mm ID.

The µBondapak C_{18} column was employed only after we found that a few of the candidate POHCs either were not retained by or did not chromatograph well on the HC-ODS-SIL-X-1 column. In practice, the performance of a column from one source to another may vary. In addition, interlaboratory differences may occur that are attributed to the handling and history of the column. Once a column is selected, its performance should be monitored throughout the study.

Rather than attempt to establish one rigid set of HPLC operating conditions, our strategy was to identify various procedural options that would allow determination of a broad range of compound types. Thus, we investigated numerous isocratic and gradient elution programs with acetonitrile/water mobile phase. In the determination of several POHCs (including the phenoxyacetic acids), the eluent was acidified. The wavelength of UV detection was also varied to optimize sensitivity.

Optimization and Calibration of the HPLC/UV Procedures

The POHCs were grouped into classes of compounds and submitted for HPLC analysis. Initially, we analyzed standard mixtures of candidate POHCs to establish solvent programs suitable for the determination of a variety of compounds. At that time the UV detector was set to monitor absorbances at 254 nm. Various chromatographic conditions were evaluated and modified until the elution rate and the resolution were optimized. The various procedures (options) are:

Option 1--Perkin-Elmer HC-ODS-SIL-X-1, 10-μm particle size, 25 cm long x 2.6-mm ID

Option 1A--Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 5 min; 10 to 100% B in 35 min; 100% B, 10 min
Solvent Flow Rate: 1.0 mL/min

Option 1B--Solvent A: 1% (v/v) acetic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 10 min; 20 to 50% B in 10 min; 50% B, 5 min
Solvent Flow Rate: 2 mL/min

Option 1C--Solvent A: 1% (v/v) acetic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 2 min; 10 to 100% B in 18 min
Solvent Flow Rate: 2 mL/min

Option 2--Waters Associates μBondapak C_{18}, 10-μm particle size, 30 cm long x 3.9-mm ID

Option 2A--Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 2% B, isocratic
Solvent Flow Rate: 1 mL/min

Option 2C--Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 0 min; 20 to 100% B in 20 min; 100% B, 10 min
Solvent Flow Rate: 1 mL/min

Option 2E--Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, isocratic
Solvent Flow Rate: 1 mL/min

In subsequent work, the UV spectra of the candidate POHCs were determined on a Cary Model 17 spectrophotometer to establish an absorption maximum in the range from 190 to 400 nm that would be a suitable alternate wavelength for quantifying each POHC by HPLC/UV.

As in the GC/FID and GC/MS analyses, calibration curves were prepared for each compound by plotting the absorbance as a function of the injected quantity of the compound.

HPLC/UV Quality-Control Procedures

As in the GC investigations, we determined the precision of determinations with replicate injections of standard solutions of the analytes. The precision of analysis was determined for only a representative group of the compounds investigated by HPLC. An internal standard was not used in the HPLC/UV determinations. In practice, not all POHCs will be found in a sample. Thus, after the POHCs in the sample are identified, an appropriate internal standard can be selected and then added to improve the quantification of POHCs.

SECTION 5

RESULTS AND DISCUSSION OF THE DEVELOPMENT OF GENERALIZED ANALYTICAL METHODS

GC/FID AND GC/MS ANALYSIS

General Considerations

In Table 1 we present the GC/FID results. The retention time and on-column detection limit are given for each compound. The compounds are listed in the order of their elution from the GC column. Retention times are relative to that observed for the internal standard, anthracene-d_{10}. The on-column detection limit is the quantity of each analyte that was estimated to yield an FID response of about twice the background signal; about three-fourths of the detection limits were in the subnanogram range. Reference chromatograms and calibration curves, which appear in Appendix A, have also been cited in Table 1.

Appendix A contains chromatograms of seven different POHC mixtures (the chromatograms cited in Table 1) and a chromatogram of a mixture of all of the candidate POHCs investigated by GC/FID (Figure A-37). The chromatograms demonstrate the observed absolute retention times, the peak shapes, and any shifts in the base line that occurred. Although no two of the candidate POHCs may coexist in a field situation and, therefore, may not require simultaneous determination, the chromatogram of the compound mixture demonstrates the resolving power of the capillary column in general.

Each reference calibration curve given in Appendix A and cited in Table 1 is a point-to-point plot (solid line) of FID response as a function of the quantity of the analyte on the GC column. Each plot can be used to estimate the sensitivity expected in the determination of a particular analyte. In generating these curves, we made no attempt to determine the upper limit of the linear range of determinations. However, each plot serves to demonstrate the linearity of FID response within the range of quantities investigated. A laboratory that uses these methods will have to generate its own calibration curves, which may differ slightly from the ones given in this report. Our calibration curves will serve as a guide.

Also, with each calibration curve is the least-squares plot (a broken line) based on the linear-regression analysis of FID response versus concentration of analyte. Linear-regression analysis of the data typically gave correlation coefficients of $\geqslant 0.9900$.

TABLE 1. SUMMARY OF GC/FID DETERMINATIONS OF CANDIDATE POHCs

Compound	Relative retention time[a]	On-column detection limit, ng	Appendix A Reference chromatogram	Appendix A Reference calibration curve
Methylhydrazine	0.0645	0.4	A-15	--[b]
Ethylenediamine	0.0842	0.4	A-15	A-16
N-Nitroso-*N*-methylethylamine	0.181	0.6	A-15	A-17
Malononitrile	0.200	0.6	A-15	A-18
Dimethyl sulfate	0.207	5.0	A-7	A-8
1,3-Dichloro-2-propanol	0.233	0.6	A-1	A-2
N-Nitrosodiethylamine	0.241	0.2	A-22	A-23
Methanesulfonic acid ethyl ester	0.265	0.7	A-12	A-13
N-Nitroso-*N*-methylurethane	0.266	2.0	A-30	--[b]
Pentachloroethane	0.306	1.0	A-1	A-3
Benzyl chloride	0.343	0.2	A-1	A-4
N-Nitrosopyrrolidine	0.411	0.2	A-15	A-17
2,6-Dichlorophenol	0.526	2.0	A-30	A-31
4-Chloroaniline	0.528	0.2	A-22	A-25
N-Nitrosodibutylamine	0.585	0.2	A-22	A-26
Safrole	0.606	0.3	A-33	A-34
3,4-Diaminotoluene	0.626	0.4	A-22	A-27
1,2,4,5-Tetrachlorobenzene	0.643	0.5	A-1	A-5
Nicotine	0.658	0.4	A-33	A-35
2,4,5-Trichlorophenol	0.666	2.0	A-30	A-32
2,4-Diaminotoluene	0.695	2.0	A-22	A-28
2,6-Diaminotoluene	0.697	0.1	A-15	A-19
1,4-Naphthoquinone	0.716	0.4	A-7	A-9
p-Dinitrobenzene	0.734	0.5	A-15	A-20
m-Dinitrobenzene	0.748	0.1	A-22	A-29
Pentachlorobenzene	0.807	0.7	A-1	A-6
alpha-Naphthylamine	0.812	0.2	A-12	A-14
p-Nitroaniline	0.880	0.5	A-15	A-21
2-Acetamidofluorene	1.38	0.4	A-33	A-36
9,10-Dimethyl-1,2-benzanthracene	1.60	1.0	A-7	A-10
Dibenz[a,j]acridine	1.93	0.8	A-7	A-11

[a] Relative to the retention time of anthracene-d_{10}; ≃16 min.

[b] Calibration curve was not included in the appendix because of poor resolution of the compound.

Table 2 summarizes the GC/MS determinations. As in Table 1, the retention times are given relative to the internal standard, anthracene-d_{10}. Table 2 also lists the five most abundant mass fragments of each compound and, moreover, specifies the mass of the ion of each compound that was used for the establishment of detection limits and for the generation of calibration curves. The detection limits are the quantities of the analytes that were estimated to yield ion currents (of the selected ions) corresponding to about twice the background ion currents. Typical values of the detection limits were 1 to 5 ng.

Reference ion chromatograms, calibration curves, and mass spectra are cited in Table 2. The mass spectra are presented in Appendix B along with the reference chromatograms and calibration curves. One reference chromatogram (Figure B-64) is for the determination of a mixture of all of the compounds investigated by GC/MS.

In Table 3 we present the results of triplicate GC/FID determinations of approximately 0.05-µg quantities of all of the candidate POHCs listed in Table 1 except the hydrazines. The calculated values of the SD and RSD in Table 3 indicate that most GC/FID determinations gave acceptable precision. RSDs greater than about 5% were, however, obtained for several of the compounds--*N*-nitrosodiethylamine, *N*-nitroso-*N*-methylurethane, methanesulfonic acid ethyl ester, pentachloroethane, benzyl chloride, 2,6-dichlorophenol, and 1,2,4,5-tetrachlorobenzene. The less precise determinations were the result of anomalously low responses obtained with the first in the series of three determinations for each of these compounds. Perhaps at least one injection was required to condition the GC column and thereby to prevent loss of the compounds in subsequent injections.

In Table 4 we present the results of triplicate GC/MS determinations of about 0.1-µg quantities of selected POHCs listed in Table 2. In general, the GC/MS determinations were less precise than the GC/FID determinations. About two-thirds of the compounds were, however, determined with an RSD of about <5%. Several of the compounds for which we obtained relatively imprecise determinations by GC/FID were also found to yield RSDs >5% by GC/MS; these included tetrachlorobenzene, pentachloroethane, and benzyl chloride.

POHCs Not Amenable to GC/FID and GC/MS Analysis

Several compounds determined by GC/FID were not determined by GC/MS. These compounds--methylhydrazine, dimethylhydrazine, and ethylenediamine--were volatile enough to be partially swept from the splitless injector of the GC/MS system along with the solvent and thus could not be determined. It is likely that these compounds could be determined, with some loss of sensitivity, by GC/MS with split injection techniques.

TABLE 2. SUMMARY OF GC/MS DETERMINATIONS OF CANDIDATE POHCs

Compound	Relative retention time[a]	On-column detection limit, ng	Mol wt	Masses of characteristic EI ions (relative abundance)					Appendix B		
				1	2	3	4	5	Reference chromatogram	Reference mass spectrum	Reference calibration curve
N-Nitroso-*N*-methylethylamine	0.148	4.8	88	88(100)	42(93)	43(46)	56(24)	71(13)	B-41	B-42	B-43
Malononitrile	0.187	5.6	66	66(100)	65(12)	64(9)	67(5)	50(5)	B-41	B-50	--[b]
1,3-Dichloro-2-propanol	0.200	6.1	129	79(100)	81(38)	43(27)	49(20)	42(8)	B-1	B-2	B-3
N-Nitrosodiethylamine	0.206	2.7	102	102(100)	42(68)	44(60)	56(56)	57(36)	B-26	B-27	B-28
Dimethyl sulfate	0.235	4.0	126	95(100)	96(76)	66(28)	79(20)	65(16)	B-12	B-13	B-14
N-Nitroso-*N*-methylurethane	0.259	23	132	43(100)	96(76)	66(28)	79(20)	65(10)	B-51	B-52	B-53
Pentachloroethane	0.277	1.2	202	117(100)	119(87)	167(82)	165(65)	169(41)	B-1	B-4	B-5
Methanesulfonic acid ethyl ester	0.298	5.2	124	79(100)	109(78)	97(26)	80(19)	65(14)	B-21	B-22	B-23
Benzyl chloride	0.316	0.72	126	91(100)	126(16)	65(16)	63(11)	89(9)	B-1	B-6	B-7
N-Nitrosopyrrolidine	0.374	1.9	100	100(100)	41(61)	42(58)	68(16)	43(14)	B-26	B-29	B-30
4-Chloroaniline	0.503	1.9	128	127(100)	65(51)	129(38)	92(29)	100(30)	B-26	B-31	B-32
N-Nitrosodibutylamine	0.568	4.8	154	84(100)	57(73)	41(61)	42(40)	99(25)	B-26	B-33	B-34
2,6-Dichlorophenol	0.582	1.7	163	162(100)	164(62)	63(58)	98(34)	99(15)	B-51	B-54	B-55
3,4-Diaminotoluene	0.600	10	122	122(100)	121(71)	94(42)	77(22)	106(21)	B-26	B-35	B-36
Safrole	0.620	0.092	162	162(100)	104(78)	77(62)	131(60)	135(36)	B-58	B-59	B-60
1,2,4,5-Tetrachlorobenzene	0.632	1.3	216	216(100)	214(85)	218(52)	74(37)	181(24)	B-1	B-8	B-9
Nicotine	0.673	4.2	162	84(100)	133(38)	42(21)	162(19)	161(18)	B-58	B-61	B-62
2,4-Diaminotoluene	0.677	10	122	121(100)	122(90)	94(29)	77(19)	105(16)	B-26	B-37	B-38
2,6-Diaminotoluene	0.696	2.4	122	122(100)	121(63)	104(36)	94(33)	106(20)	B-41	B-44	B-45
p-Dinitrobenzene	0.723	1.5	168	168(100)	76(82)	50(80)	75(78)	122(34)	B-41	B-46	B-47
m-Dinitrobenzene	0.735	1.5	168	168(100)	76(92)	50(82)	75(75)	122(32)	B-26	B-39	B-40
2,4,5-Trichlorophenol	0.735	2.2	197	198(100)	196(96)	97(58)	200(31)	132(29)	B-51	B-56	B-57
1,4-Naphthoquinone	0.741	3.6	158	158(100)	102(67)	104(66)	76(62)	130(45)	B-12	B-15	B-16
Pentachlorobenzene	0.787	1.0	250	250(100)	252(62)	248(62)	108(41)	54(21)	B-1	B-10	B-11
alpha-Naphthylamine	0.824	0.33	143	143(100)	115(51)	116(29)	144(12)	89(11)	B-21	B-24	B-25
p-Nitroaniline	0.871	5.1	138	138(100)	65(85)	108(84)	92(40)	80(24)	B-41	B-48	B-49
2-Acetamidofluorene	1.41	3.7	223	181(100)	180(82)	223(62)	152(37)	153(19)	B-58	B-63	--[b]
9,10-Dimethyl-1,2-benzanthracene	1.55	4.9	256	256(100)	241(54)	239(36)	240(36)	257(19)	B-12	B-17	B-18
Dibenz[a,j]acridine	1.96	12	279	279(100)	280(38)	277(19)	125(14)	139(11)	B-12	B-19	B-20

[a] Relative to the retention time of anthracene-d_{10}, ≈16 min.

[b] Calibration curve was not included in the appendix because of poor resolution of the compound.

TABLE 3. PRECISION OF GC/FID DETERMINATIONS

Compound	Quantity on column, ng	RRF[a]		
		Mean	SD	RSD, %
2-Acetamidofluorene	47.1	0.698	0.011	1.6
Benzyl chloride	51.1	0.864	0.059	6.8
4-Chloroaniline	57.6	0.657	0.027	4.1
2,4-Diaminotoluene	65.0	0.691	0.0085	1.2
2,6-Diaminotoluene	60.5	0.618	0.0035	0.57
3,4-Diaminotoluene	64.0	0.705	0.012	1.7
Dibenz[a,j]acridine	43.7	0.801	0.0070	0.87
2,6-Dichlorophenol	53.1	0.396	0.026	6.6
1,3-Dichloro-2-propanol	55.6	0.234	0.013	5.5
9,10-Dimethyl-1,2-benzanthracene	48.6	1.06	0.0000	0.00
Dimethylsulfate	62.5	0.0476	0.0019	4.0
m-Dinitrobenzene	46.7	0.554	0.0036	0.65
p-Dinitrobenzene	63.5	0.328	0.0000	0.00
Ethylenediamine	64.5	0.0387	0.0012	3.1
Malononitrile	66.0	0.828	0.0037	4.5
Methanesulfonic acid ethyl ester	56.1	0.243	0.026	11
Methylhydrazine	67.4	0.202	0.011	5.4
1,4-Naphthoquinone	44.2	0.438	0.025	5.7
alpha-Naphthylamine	49.6	1.10	0.021	1.9
Nicotine	56.6	0.618	0.0083	1.3
p-Nitroaniline	66.0	0.561	0.0092	1.6
N-Nitrosodibutylamine	61.0	0.695	0.027	3.9
N-Nitrosodiethylamine	59.6	0.609	0.050	8.2
N-Nitroso-*N*-methylethylamine	60.5	0.467	0.020	4.3
N-Nitroso-*N*-methylurethane	43.2	0.182	0.012	6.6
N-Nitrosopyrrolidine	78.4	0.558	0.024	4.3
Pentachlorobenzene	51.6	0.359	0.021	5.8
Pentachloroethane	69.5	0.161	0.012	7.5
Safrole	48.6	0.722	0.0093	1.3
1,2,4,5-Tetrachlorobenzene	48.6	0.427	0.0300	7.0
2,4,5-Trichlorophenol	51.1	0.414	0.0050	1.4

[a] RRF = $(A_s C_{is})/(A_{is} C_s)$

TABLE 4. PRECISION OF GC/MS DETERMINATIONS

Compound	Quantity injected, ng	RRF[a] Mean	SD	RSD, %
2-Acetamidofluorene	95.3	0.151	0.012	7.9
Benzyl chloride	103	0.445	0.057	13
4-Chloroaniline	116	0.101	0.010	9.9
2,4-Diaminotoluene	131	0.227	0.0044	1.9
2,6-Diaminotoluene	122	0.128	0.0000	0.00
3,4-Diaminotoluene	129	0.110	0.0040	3.6
Dibenz[a,j]acridine	88.2	0.252	0.023	9.1
2,6-Dichlorophenol	107	0.199	0.0060	3.0
1,3-Dichloro-2-propanol	112	0.144	0.0067	4.7
9,10-Dimethyl-1,2-benzanthracene	97.6	0.0293	0.0048	16
Dimethyl sulfate	126	0.138	0.0080	5.8
m-Dinitrobenzene	94.5	0.157	0.0085	5.4
p-Dinitrobenzene	128	0.0490	0.00067	1.4
Methanesulfonic acid ethyl ester	113	0.216	0.0081	3.8
1,4-Naphthoquinone	88.8	0.316	0.011	3.5
alpha-Naphthylamine	100	0.660	0.011	1.7
Nicotine	114	0.257	0.024	9.3
p-Nitroaniline	133	0.0931	0.0057	6.1
N-Nitrosodibutylamine	123	0.214	0.020	9.3
N-Nitroso-*N*-methylethylamine	122	0.0820	0.0018	2.2
N-Nitroso-*N*-methylurethane	86.9	0.118	0.0047	4.0
N-Nitrosopyrrolidine	158	0.144	0.013	9.0
Pentachlorobenzene	104	0.184	0.0053	2.9
Pentachloroethane	140	0.0970	0.0085	8.8
Safrole	98.1	0.152	0.0032	2.1
1,2,4,5-Tetrachlorobenzene	97.6	0.211	0.011	5.2
2,4,5-Trichlorophenol	103	0.288	0.010	3.5

[a] RRF = $(A_{is}C_{is})/(A_{is}C_{s})$

Some other compounds investigated could not be determined reliably by the GC/FID or GC/MS survey methods. These included maleic anhydride, thiophenol, cyclophosphamide, and o-toluidine. Apparently, these compounds were irreversibly adsorbed by the GC column or were decomposed in solution, on the column, or in the injection port.

HPLC ANALYSIS

A summary of HPLC/UV determinations is given in Table 5. A description of the generalized HPLC/UV analysis method including the various procedural options is presented in Section 4.

In Table 5, the option used in the determination of each compound is specified. Over half of the listed compounds were determined by Option 1A. Option 1B, which involved the acidification of the eluent, was instituted primarily for the determination of the phenoxyacetic acids. We observed that 4,6-dinitro-o-cresol and methyl yellow chromatographed very poorly without the inclusion of acid in the eluent; thus, Option 1C was established for the determination of these two compounds. Option 2A was suitable for the determination of N-nitroso-N-methylurea, and Option 2B was suitable for saccharin. (Option 2C was used for the determination of other compounds discussed later.) For some of the compounds, it is likely that another option--either one of the other options listed here or a new set of operating conditions--would have given results comparable to those presented in Table 5.

The application of the specified procedures yielded the retention times and detection limits given in Table 5. For most of the compounds listed, the initial determinations were made at a detector wavelength of 254 nm, the wavelength of maximum absorbance for the phenyl functional group. After we had selected optimum wavelengths for analysis, we redetermined some of the compounds to establish lower detection limits. The limits established for the optimum wavelengths were typically <10 ng and usually about a factor of 10 lower than the limits at 254 nm.

Table 5 cites the reference chromatograms, UV spectra, and calibration curves generated for the compounds listed. The chromatograms were obtained for 2- to 10-μg quantities of each analyte injected onto the appropriate HPLC column. The calibration curves were plotted with the GC/MS data system as described previously for the GC determinations. Correlation coefficients were typically >0.999, with a few exceptions. For some exceptions, such as phenol, we obtained calibration curves that were nonlinear. Because these curves nonetheless appeared to be useful in determining the substance with reasonable accuracy, we did not consider it necessary to determine these substances on other HPLC columns or with alternative solvent programs.

TABLE 5. SUMMARY OF HPLC/UV DETERMINATIONS OF CANDIDATE POHCs

					Appendix C		
Compound	Procedural option[a]	Retention time, min	Wavelength of detection, nm	On-column detection limit, ng	Reference chromatogram	Reference UV spectrum	Reference calibration curve
Streptozotocin	1A	1.4	254 / 230	2	C-1	C-2	C-3 / C-4
Phenol	1A	5.4	254 / 280	80	C-5	C-6	C-7 / C-8
4-Nitrophenol	1A	9.5	254 / 280	50 / 6	C-9	C-10	C-11 / C-12
o-Chlorophenol	1A	12.4	254 / 280	70 / 6	C-13	C-14	C-15 / C-16
Acetophenetidine	1A	12.6	254 / 248	1	C-17	C-18	C-19
5-Nitro-*o*-toluidine	1A	14.3	254 / 253	1	C-20	C-21	C-22
Tetramethylthiuram disulfide	1A	16.3	254 / 280	1	C-23	C-24	C-25
4-Chloro-*m*-cresol	1A	16.8	254 / 280	80 / 4	C-26	C-27	C-28 / C-29
2,4-Dichlorophenol	1A	17.6	254 / 280	100 / 2	C-30	C-31	C-32 / C-33
3-(*alpha*-Acetonylbenzyl)-4-hydroxycoumarin	1A	19.8	254 / 280	2	C-34	C-35	C-36
2,4,6-Trichlorophenol	1A	20.0	254 / 280	50 / 7	C-37	C-38	C-39 / C-40
2,3,4,6-Tetrachlorophenol	1A	21.5	254 / 280	20 / 20	C-41	C-42	C-43 / C-44
Reserpine	1A	22.7	254 / 267	30	C-45	C-46	C-47
Chlorambucil	1A	23.9	254 / 258	1	C-48	C-49	C-50
2,4-Dichlorophenoxyacetic acid	1B	7.6	254 / 284	70	C-51	C-52	C-53
2,4,5-Trichlorophenoxyacetic acid	1B	14.2	254 / 287	60	C-54	C-55	C-56
2-(2,4,5-Trichlorophenoxy)-propionic acid	1B	16.5	254 / 287	40	C-57	C-58	C-59
4,6-Dinitro-*o*-cresol	1C	7.6	378	20	C-60	C-61	C-62
Methyl yellow	1C	13.1	400	3	C-60	C-63	C-64
N-Nitroso-*N*-methylurea	2A	8.4	254 / 234	10	C-65	C-66	C-67
Saccharin	2B	3.2	254 / 224	2	C-68	C-69	C-70

[a] See Section 4, p. 11 for description of procedural options.

In addition to the compounds cited in Table 5, we found others that may be determined by the generalized HPLC/UV test procedure. Because of time constraints, the investigation of these substances was not completed; nevertheless, compounds are presented in Table 6 as potential candidates for analysis by the HPLC/UV procedure. Retention times and approximate detection limits were determined for the compounds on the basis of a limited number of injections of standard solutions. The retention times of several of the compounds--thiourea, thioacetamide, and ethylene thiourea--were uncertain because several major peaks were observed in their chromatograms. The presence of more than one major peak in the chromatogram was interpreted as an indication of gross contamination of the sample or as an indication of the decomposition of the analyte on the HPLC column. Thus, the feasibility of the application of the method to the determination of these four compounds is uncertain.

The precision of HPLC determinations for a representative group of the candidate POHCs is demonstrated by the data in Table 7. All but two compounds gave <5% RSD for triplicate determinations. The precision of the determination of acetophenetidine was biased by one value that was 15% higher than the other two. Perhaps additional determinations would have proved the high result to be a statistical outlier. The determinations of 5-nitro-*o*-toluidine yielded increasing responses with each subsequent determination; such a trend is usually indicative of column conditioning. Perhaps the response would reach a stable value after repeated injections.

TABLE 6. POTENTIAL CANDIDATES FOR ANALYSIS BY HPLC/UV

Compound	Procedural option[a]	Retention time, min	Approximate on-column detection limit,[b] ng	Wavelength of detection, nm
Trypan blue	2C	3	20	315
Epinephrine	2C	3	60	279
Thiosemicarbazide	2C	3	5	254
Thiourea	2C	≃3[c]	6	254
Thioacetamine	2C	≃4[c]	2	254
Ethylene thiourea	2C	≃4[c]	8	254
Crotonaldehyde	2C	5	1	230
Diethylstilbestrol	2C	14	4	240
Mitomycin C	1A	5	17	254
Melphalan	1A	14	10	254
3,3'-Dimethyoxybenzidine dihydrochloride	1A	≃19	9	254
Daunomycin	1B	8	75	254
Azaserine	2A	4	2	254

[a] See Section 4, page 11 for description of procedural options.

[b] Quantity injected that should yield a response of 1000 counts on the integrator.

[c] The presence of several major peaks in the chromatogram made the assignment of a retention time difficult.

TABLE 7. PRECISION OF HPLC/UV DETERMINATIONS

Compound	Quantity injected, μg	Area counts x 10^{-3}		
		Mean	SD	RSD, %
3-(*alpha*-Acetonylbenzyl)-4-hydroxycoumarin	9.39	894	8.0	0.9
Acetophenetidine	2.52	962	85	8.9
Chlorambucil	1.76	452	4.0	0.9
5-Nitro-*o*-toluidine	2.48	747	56	7.4
N-Nitroso-*N*-methylurea	4.96	108	1.0	0.8
Reserpine	7.50	58.8	2.5	4.2
Saccharin	0.977	42.7	0.66	1.5
Tetramethylthiuram disulfide	9.45	264	10	0.4

SECTION 6

DESCRIPTION OF SUPPLEMENTARY METHODS DEVELOPMENT AND OTHER TASKS

In addition to the work that was performed at Southern Research Institute, other specific tasks were carried out by Battelle-Columbus Laboratories. These tasks are listed below:

- Development of analysis methods for brucine and 2-fluoroacetamide.
- Recommendation of potentially useful air-sampling, sample-preparation, and analysis procedures for various POHCs.
- Revision of the general sample digestion procedure and specific analysis methods for the determination of metals.
- Evaluation of digestion and analysis procedures for beryllium, strontium, and vanadium.

Most of this information is historical and has been superseded by approaches in the Methods Manual. Nevertheless, we have included the results of these tasks in Appendix D.

SECTION 7

QUALITY-ASSURANCE SUMMARY

The work that was done at SoRI and presented in this report was performed under Contract 68-02-2685, Work Assignment 111. Although the project includes environmentally related measurement activities, no field samplings were analyzed. Thus, sampling procedures, chain-of-custody procedures, and spiked-sample matrixes were considered as inapplicable in the systematic review of this project. The major efforts of SoRI were to evaluate and, when necessary, modify GC/MS and HPLC/UV generalized analysis procedures for candidate POHCs. This task was accomplished with individual POHCs and mixtures of POHCs.

An internal audit of the project revealed no deficiencies in the internal quality-control checks and data processing. The relative retention times, on column detection limits, chromatograms, calibration curves, relative ion abundances, spectra, and relative standard deviations in this report will be a guide for other analytical laboratories. Because of subtle differences among laboratories and analytical instrumentation, analysts who participate in similar studies should generate data that will establish their own criteria for the analysis of POHCs.

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APPENDIX A

CHROMATOGRAMS AND CALIBRATION CURVES FOR GC/FID DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference calibration curve Figure No.
2-Acetamidofluorene	A-33	A-36
Benzyl chloride	A-1	A-4
4-Chloroaniline	A-22	A-25
2,4-Diaminotoluene	A-22	A-28
2,6-Diaminotoluene	A-15	A-19
3,4-Diaminotoluene	A-22	A-27
Dibenz[a,j]acridine	A-7	A-11
2,6-Dichlorophenol	A-30	A-31
1,3-Dichloro-2-propanol	A-1	A-2
9,10-Dimethyl-1,2-benzanthracene	A-7	A-10
Dimethyl sulfate	A-7	A-8
_m_-Dinitrobenzene	A-22	A-29
_p_-Dinitrobenzene	A-15	A-20
Ethylene diamine	A-15	A-16
Malononitrile	A-15	A-18
Methanesulfonic acid ethyl ester	A-12	A-13
Methylhydrazine	A-15	--[a]
1,4-Naphthoquinone	A-7	A-9
alpha-Naphthylamine	A-12	A-14
Nicotine	A-33	A-35
_p_-Nitroaniline	A-15	A-21
_N_-Nitrosodibutylamine	A-22	A-26
_N_-Nitrosodiethylamine	A-22	A-23
_N_-Nitroso-_N_-methylethylamine	A-15	A-17
_N_-Nitroso-_N_-methylurethane	A-30	--[a]
_N_-Nitrosopyrrolidine	A-15	A-17
Pentachlorobenzene	A-1	A-6
Pentachloroethane	A-1	A-3
Safrole	A-33	A-34
1,2,4,5-Tetrachlorobenzene	A-1	A-5
2,4,5-Trichlorophenol	A-30	A-32

[a] Calibration curve not available.

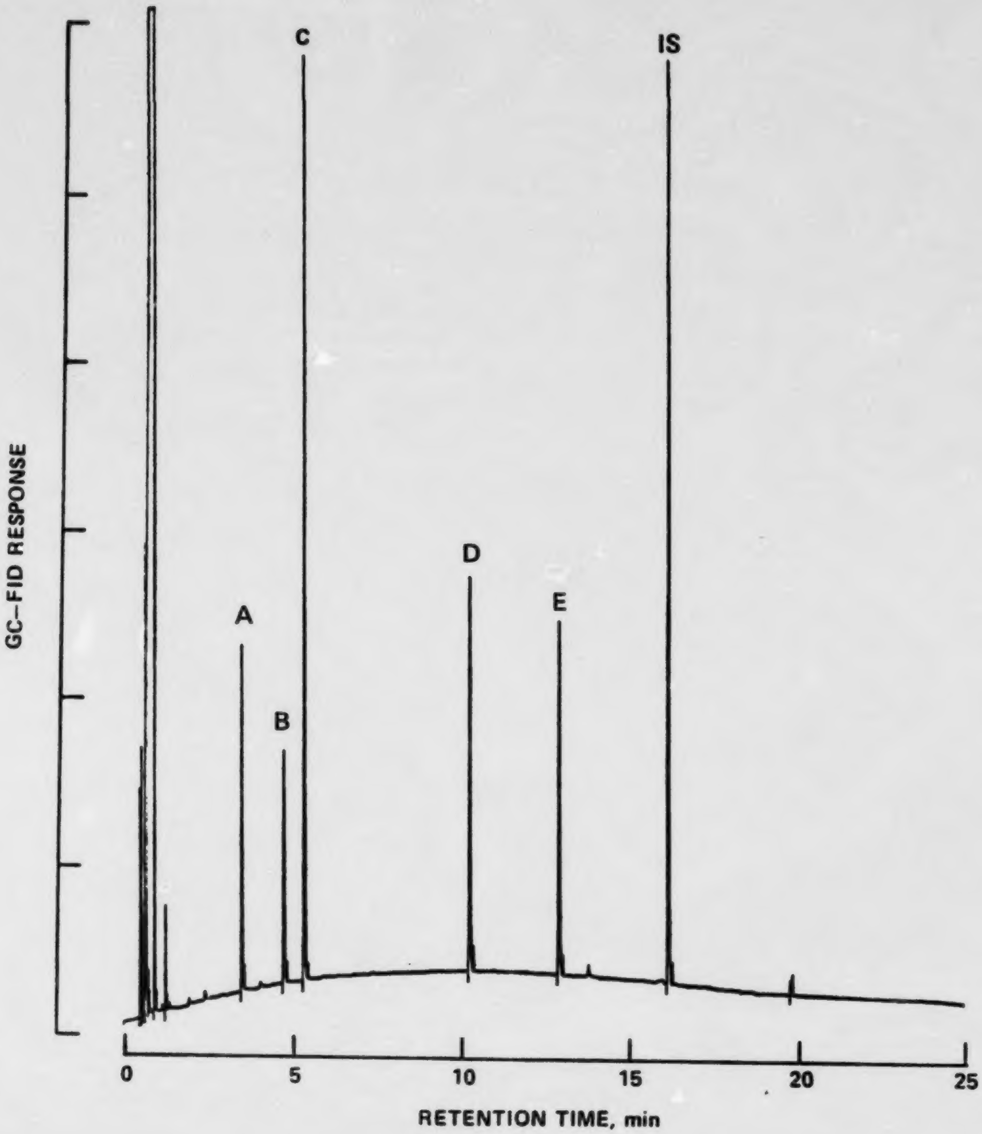

Figure A-1. Chromatogram by GC/FID for

(A) 1,3-dichloro-2-propanol(t_R = 3.8 min),
(B) pentachloroethane(t_R = 5.0 min),
(C) benzyl chloride(t_R = 5.6 min),
(D) 1,2,4,5-tetrachlorobenzene(t_R = 10.5 min), and
(E) pentachlorobenzene(t_R = 13.1 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

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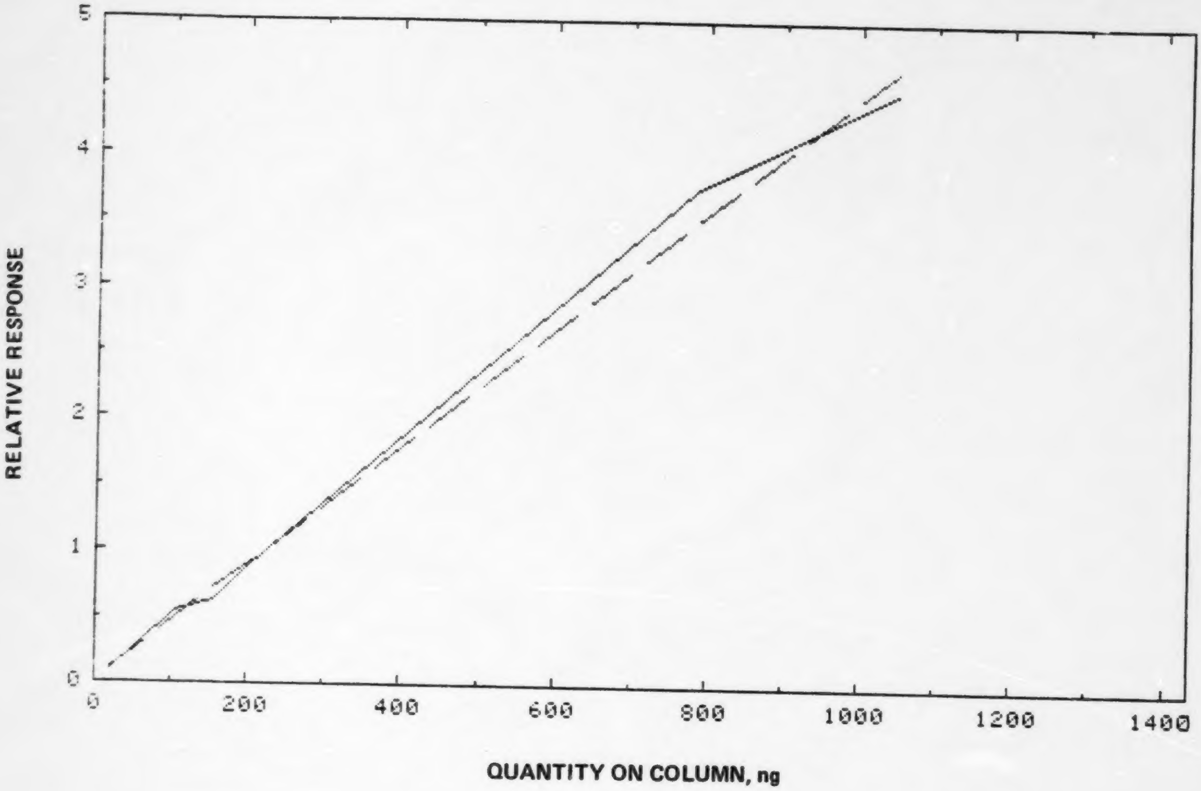

Figure A-2. Calibration curve for the determination of 1,3-dichloro-2-propanol by GC/FID.

Range: 21 - 1000 ng
Correlation coefficient: 0.997
Slope: 4.4×10^{-3}
y-Intercept: 2.4×10^{-2}

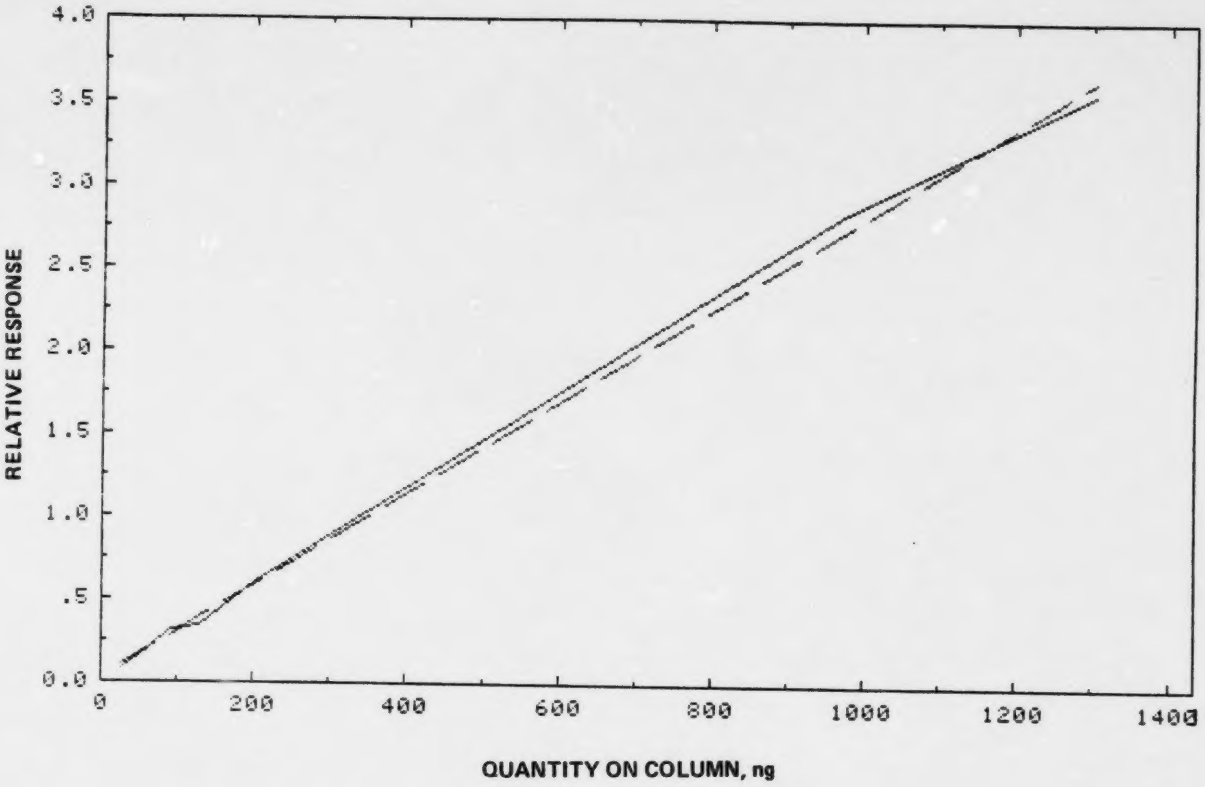

Figure A-3. Calibration curve for the determination of pentachloroethane by GC/FID.

Range: 65 - 1300 ng
Correlation coefficient: 0.999
Slope: 2.8×10^{-3}
y-Intercept: 2.9×10^{-2}

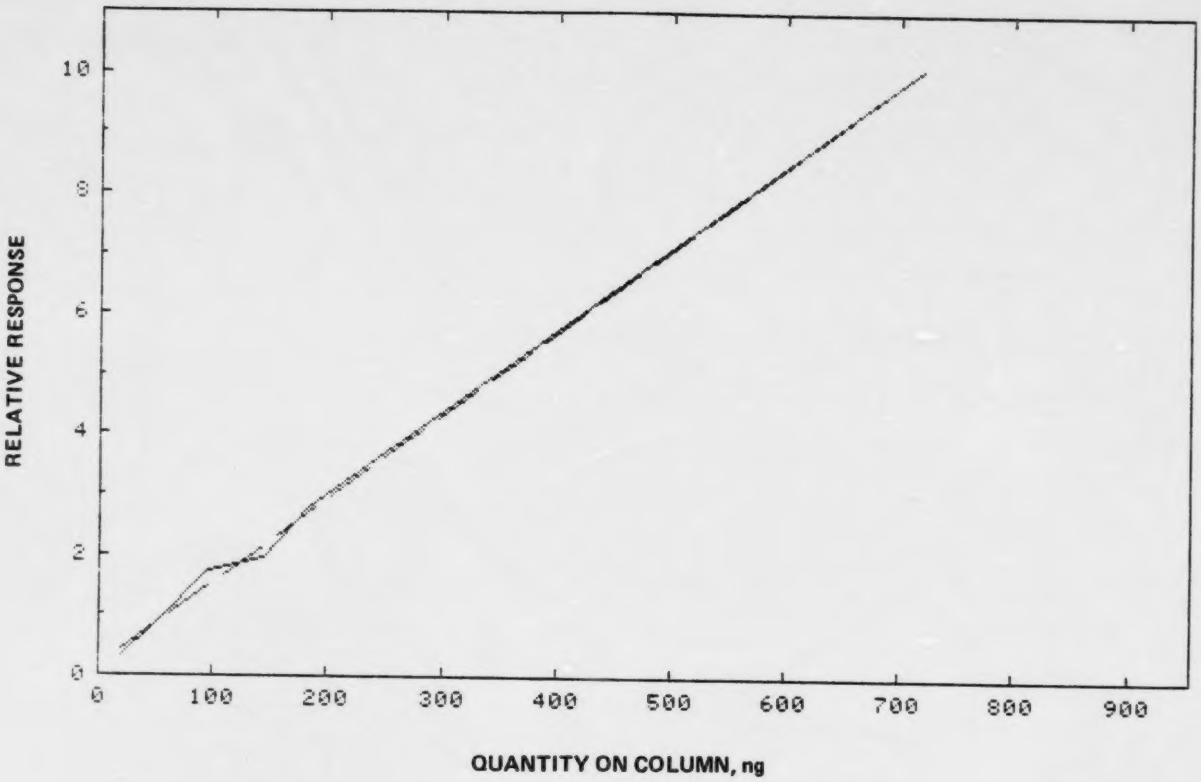

Figure A-4. Calibration curve for the determination of benzyl chloride by GC/FID.

Range: 48 - 720 ng
Correlation coefficient: 0.999
Slope: 1.4×10^{-1}
y-Intercept: 1.6×10^{-1}

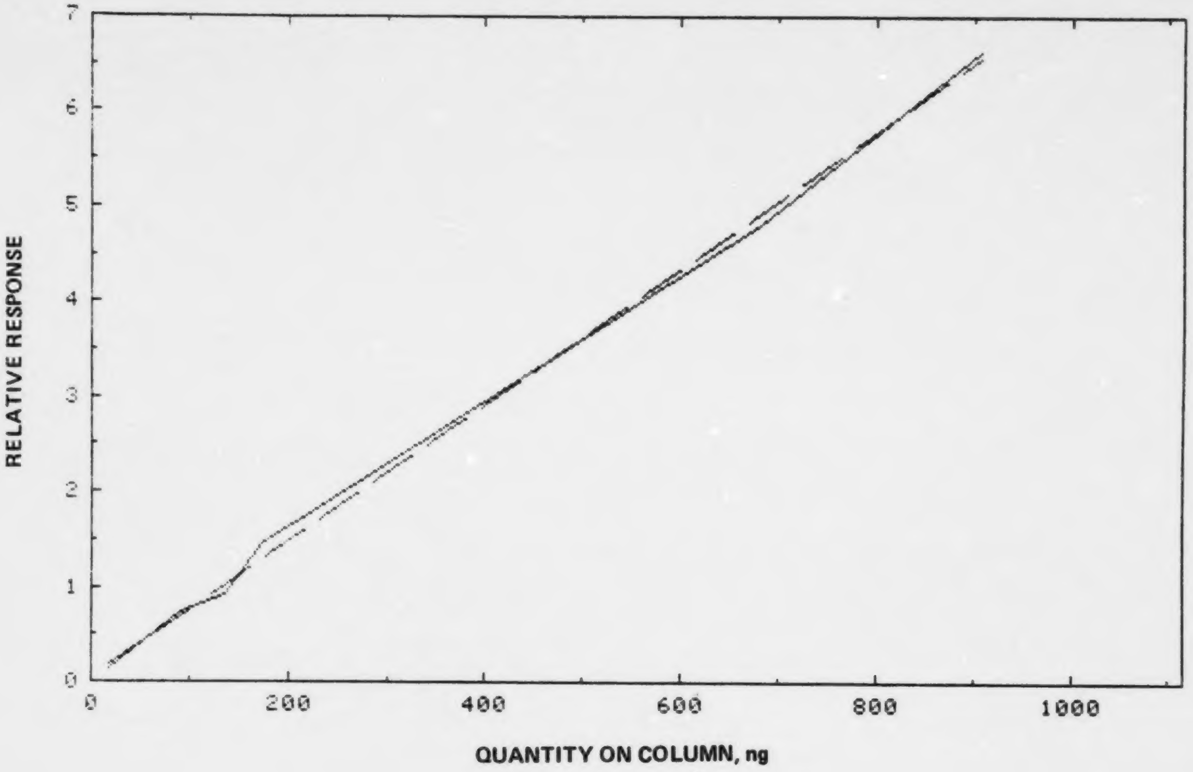

Figure A-5. Calibration curve for the determination of 1,2,4,5-tetrachlorobenzene by GC/FID.

Range: 18 - 910 ng
Correlation coefficient: 0.999
Slope: 7.2×10^{-3}
y-Intercept: 4.8×10^{-2}

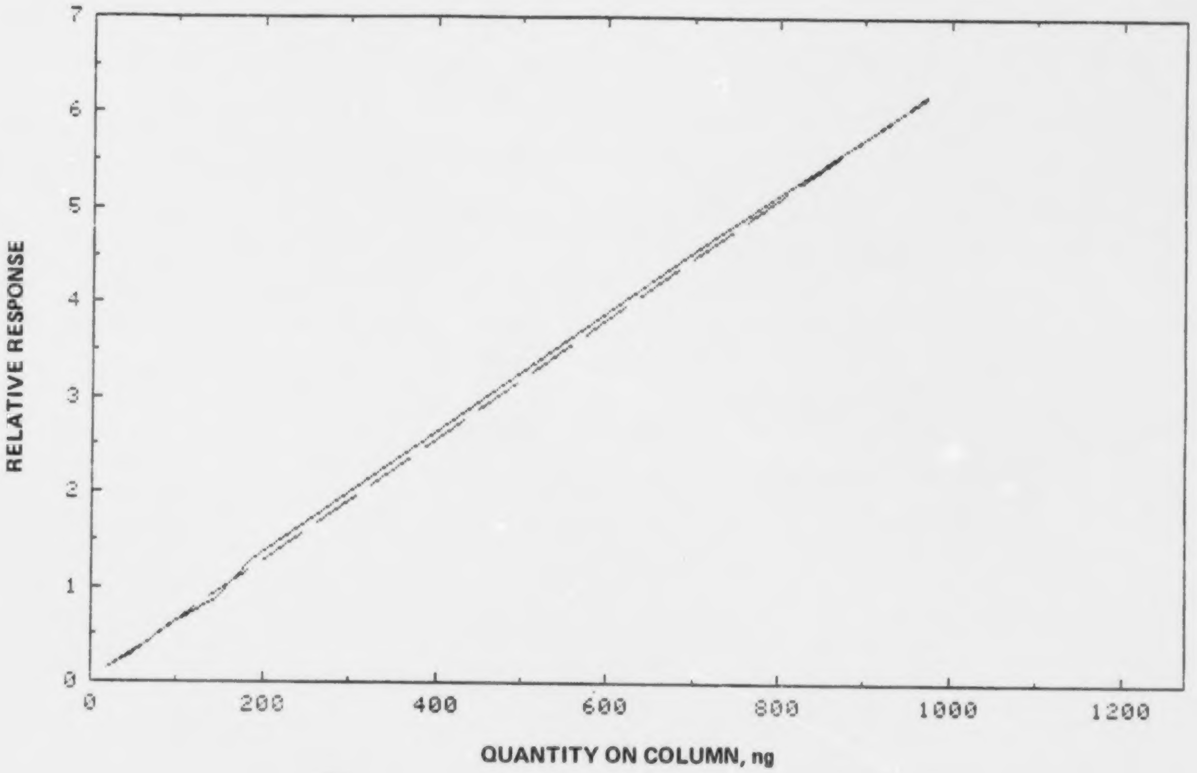

Figure A-6. Calibration curve for the determination of pentachlorobenzene by GC/FID.

Range: 19 - 970 ng
Correlation coefficient: 0.999
Slope: 6.4×10^{-3}
y-Intercept: 1.0×10^{-2}

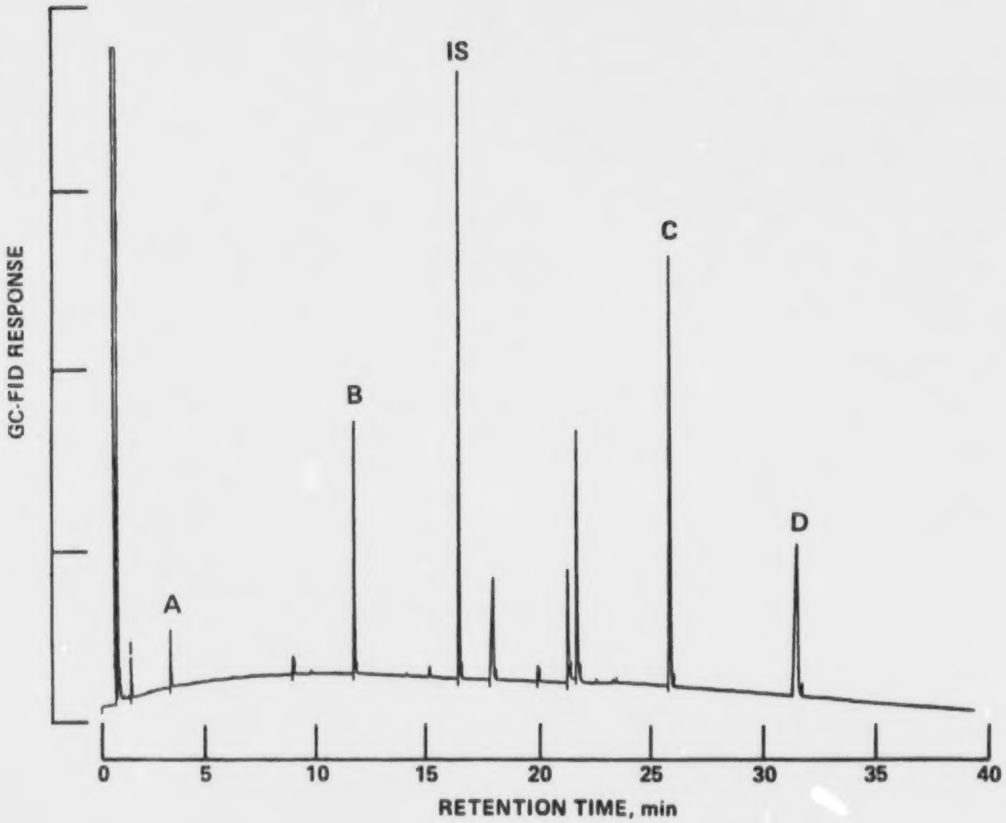

Figure A-7. Chromatogram by GC/FID for

(A) dimethyl sulfate(t_R = 3.4 min),
(B) 1,4-naphthoquinone(t_R = 11.7 min),
(C) 9,10-dimethyl-1,2-benzanthracene(t_R = 26.0 min), and
(D) dibenz[a,j]acridine(t_R = 31.5 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

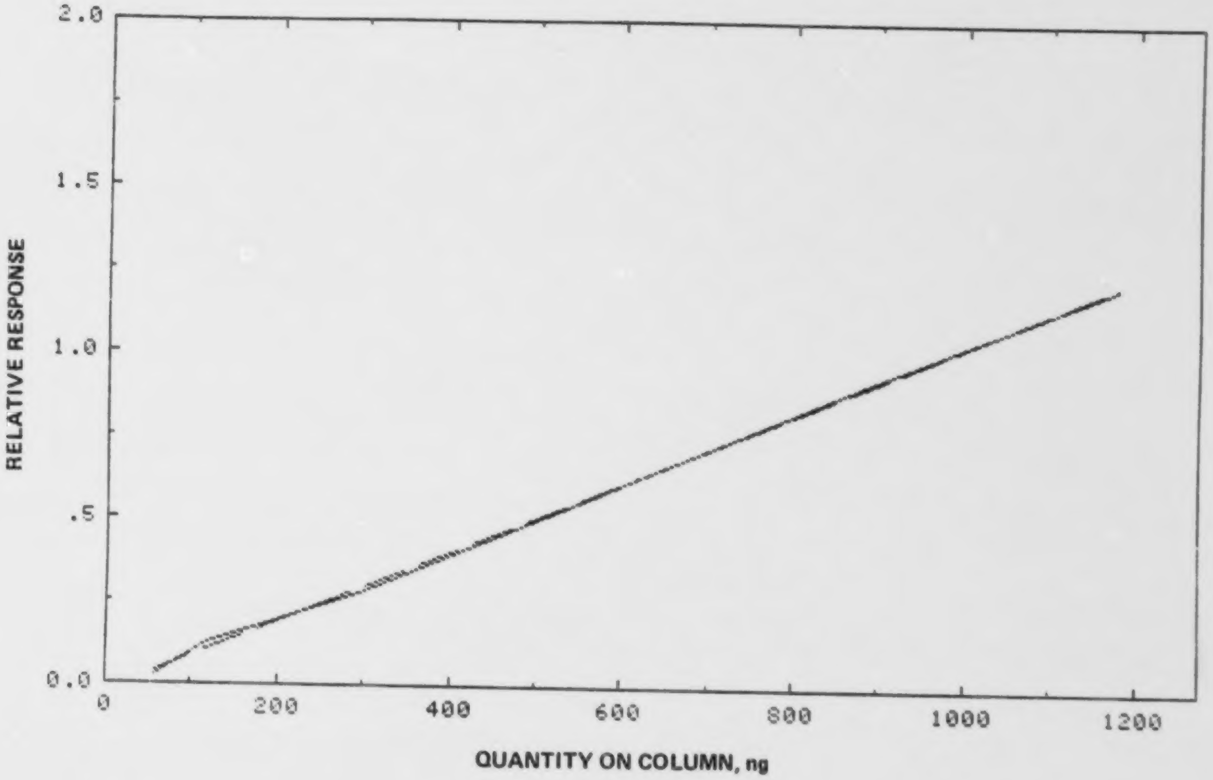

Figure A-8. Calibration curve for the determination of dimethyl sulfate by GC/FID.

Range: 120 - 1200 ng
Correlation coefficient: 0.999
Slope: 1.1×10^{-3}
y-Intercept: -2.0×10^{-2}

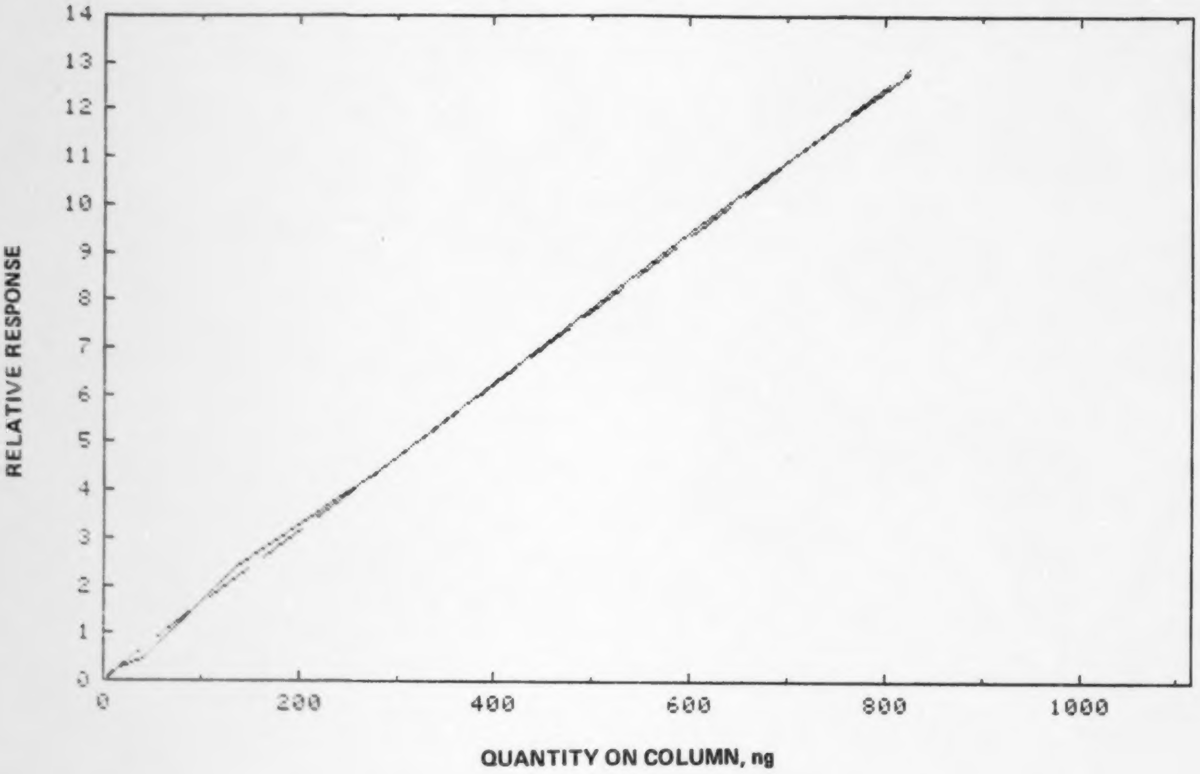

Figure A-9. Calibration curve for the determination of 1,4-naphthoquinone by GC/FID.

Range: 20 - 830 ng
Correlation coefficient: 0.999
Slope: 1.6×10^{-2}
y-Intercept: 4.0×10^{-2}

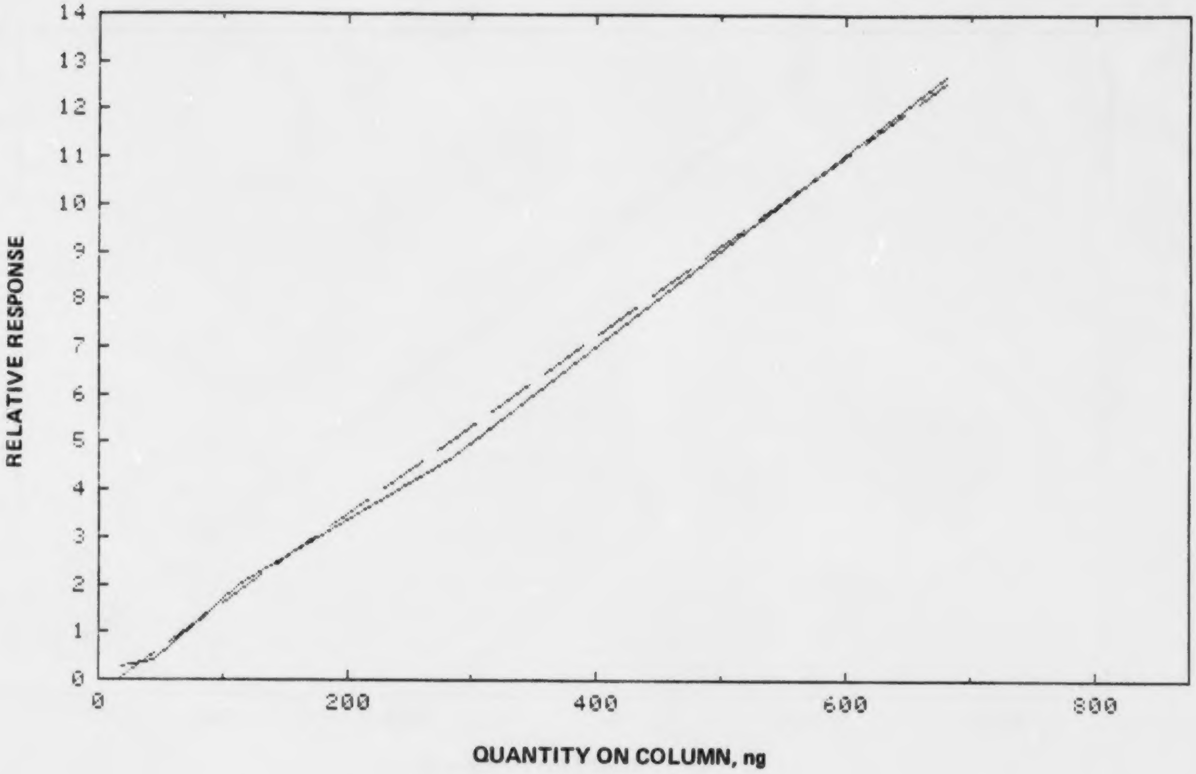

Figure A-10. Calibration curve for the determination of 9,10-dimethyl-1,2-benzanthracene by GC/FID.

Range: 46 - 680 ng
Correlation coefficient: 0.998
Slope: 1.9×10^{-2}
y-Intercept: -2.9×10^{-1}

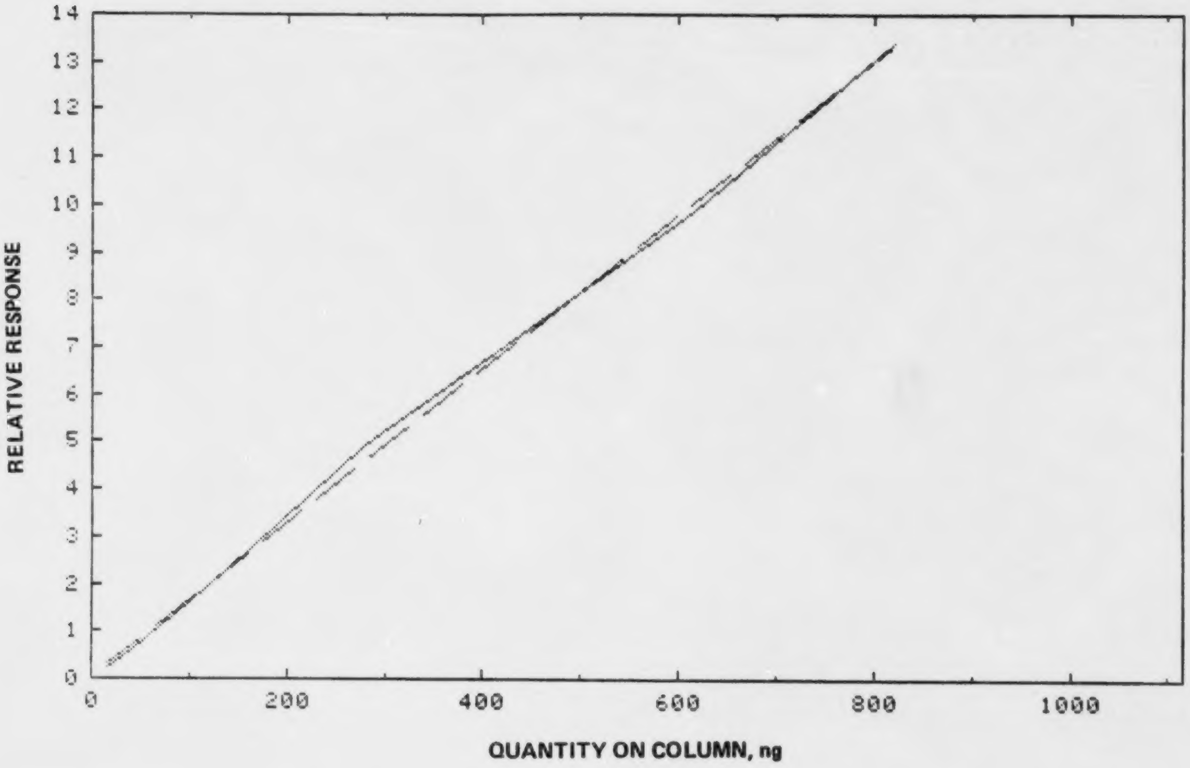

Figure A-11. Calibration curve for the determination of dibenz[a,j]acridine by GC/FID.

Range: 41 - 820 ng
Correlation coefficient: 0.999
Slope: 1.6×10^{-2}
y-Intercept: 3.6×10^{-2}

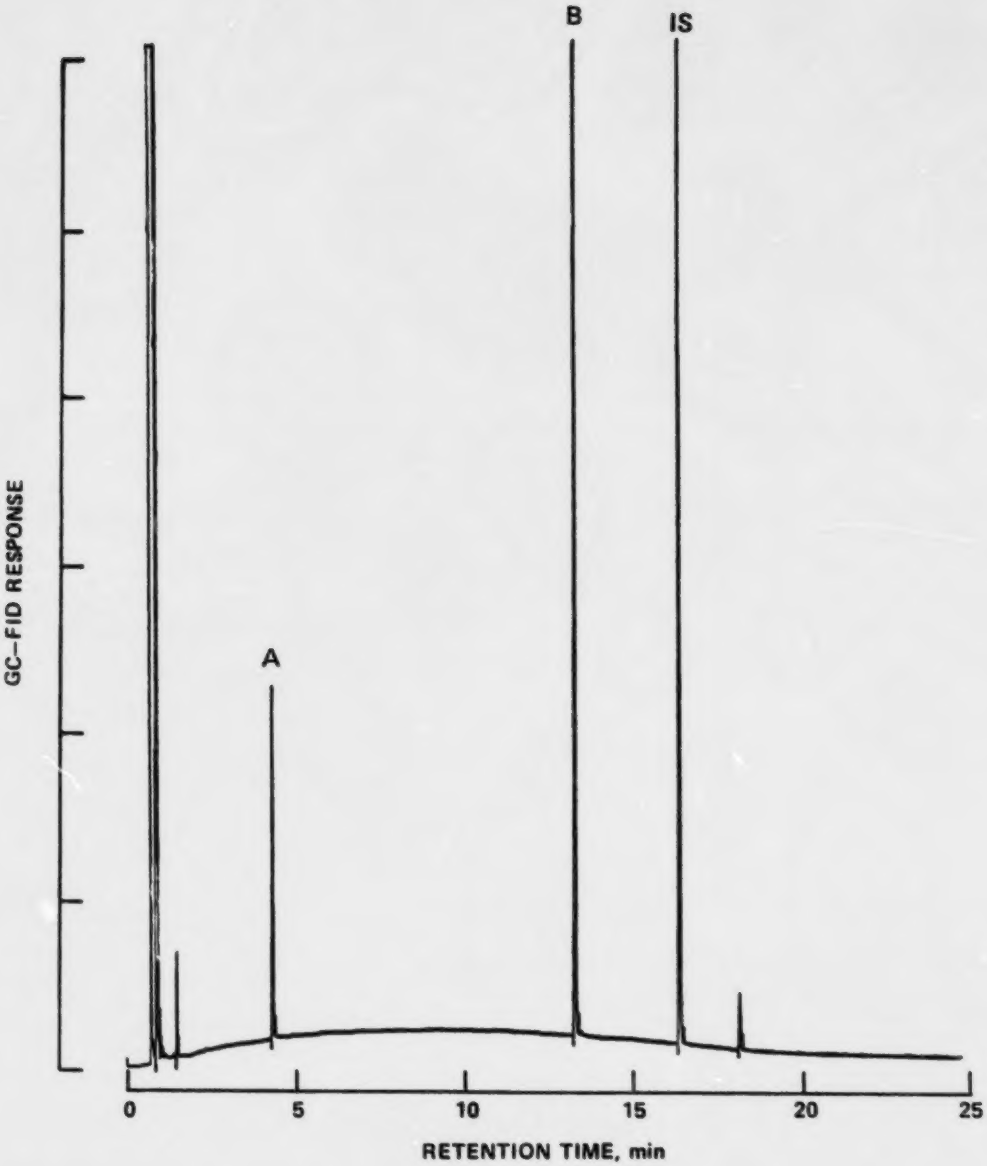

Figure A-12. Chromatogram by GC/FID for

(A) methanesulfonic acid ethyl ester(t_R = 4.6 min) and
(B) alpha-naphthylamine(t_R = 13.6 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

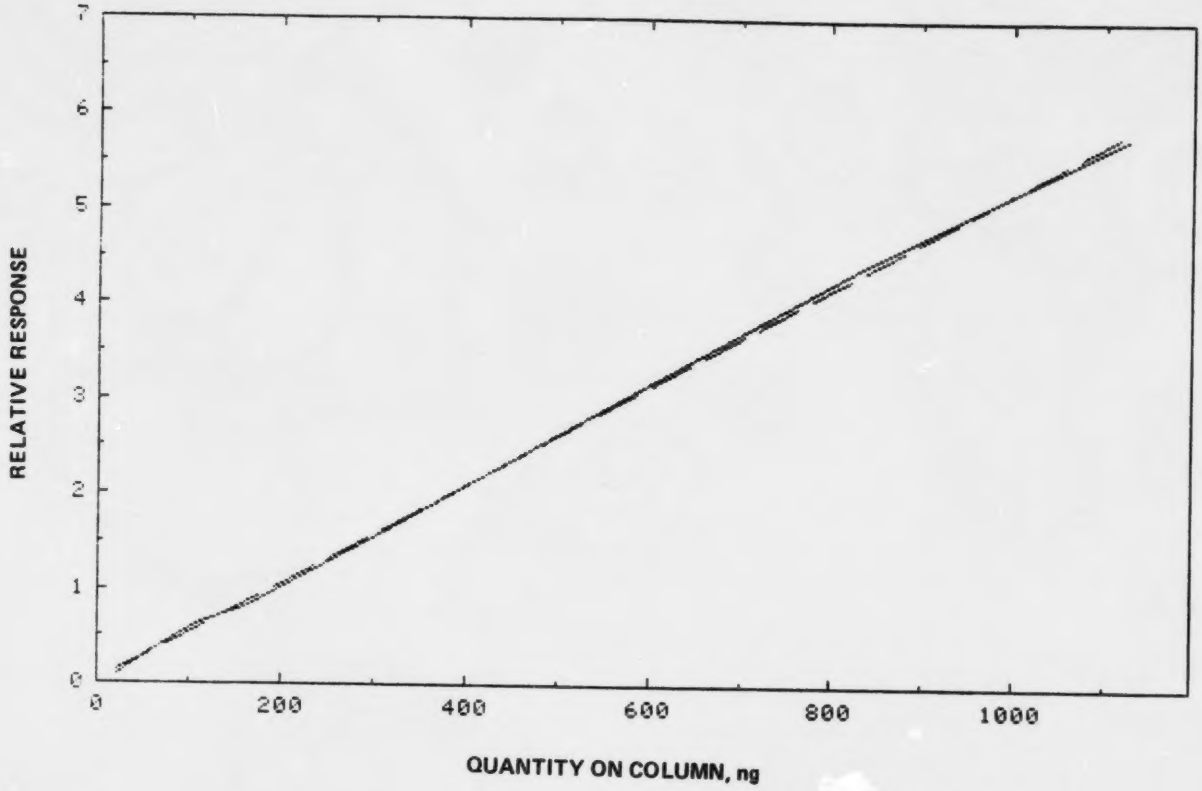

Figure A-13. Calibration curve for the determination of methanesulfonic acid ethyl ester by GC/FID.

Range: 56 - 1100 ng
Correlation coefficient: 0.999
Slope: 5.2×10^{-3}
y-Intercept: 1.6×10^{-2}

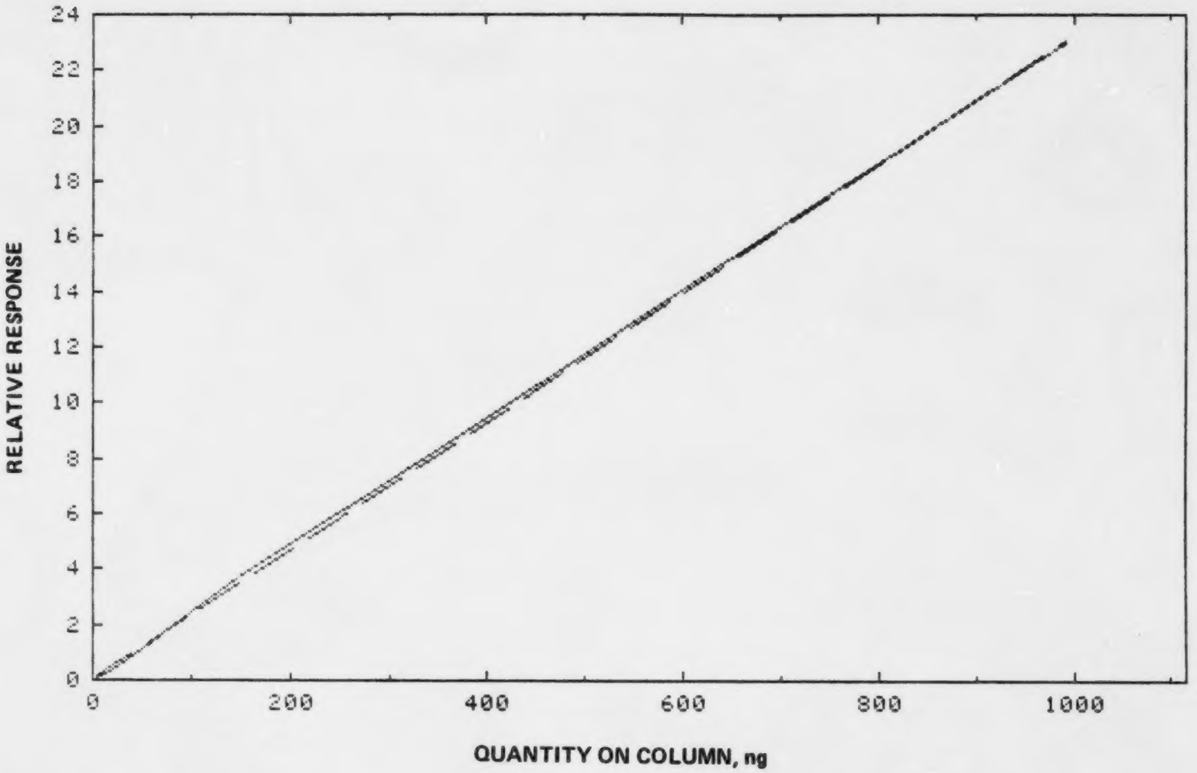

Figure A-14. Calibration curve for the determination of alpha-naphthylamine by GC/FID.

Range: 20 - 990 ng
Correlation coefficient: 0.999
Slope: 2.3×10^{-2}
y-Intercept: 6.2×10^{-2}

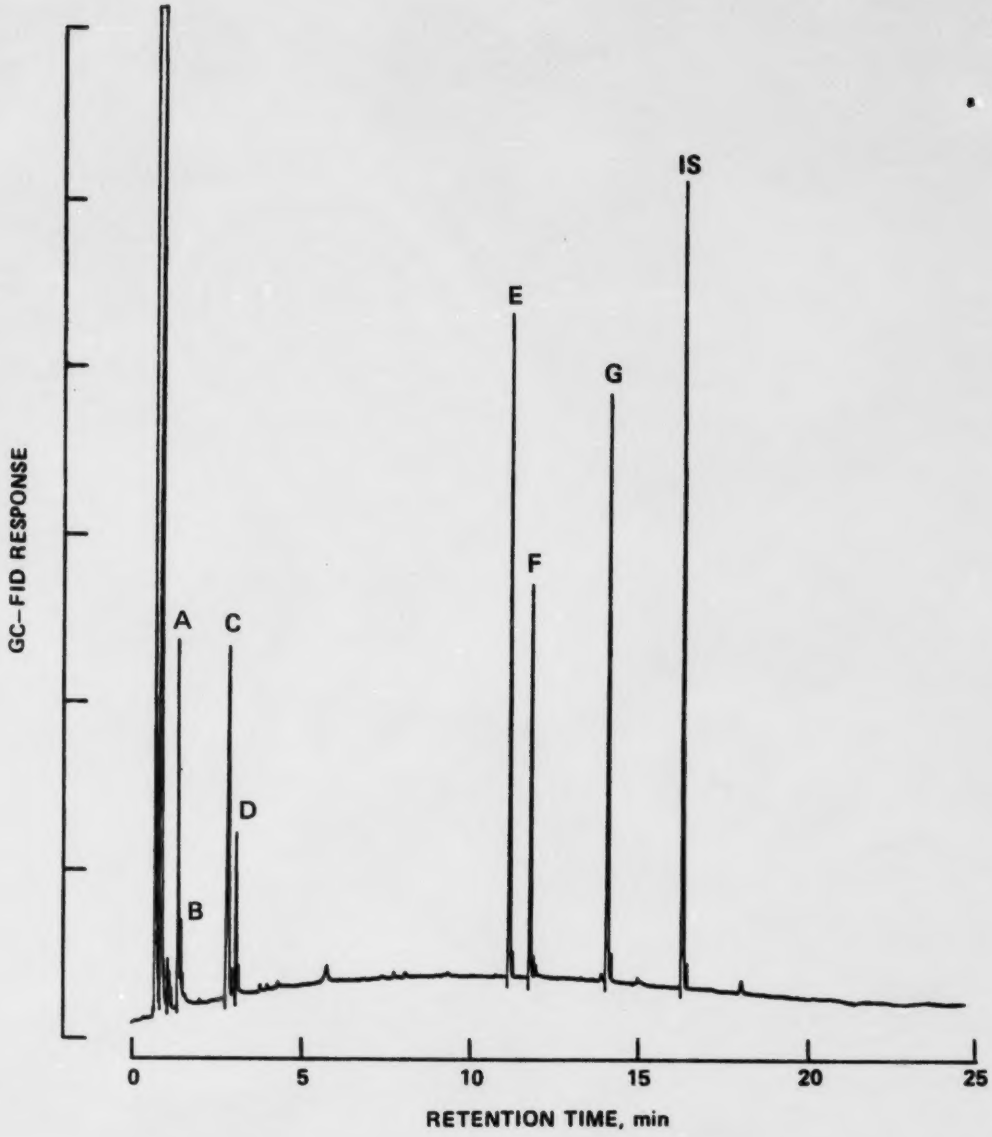

Figure A-15. Chromatogram by GC/FID for

(A) methyl hydrazine(t_R = 1.1 min),
(B) ethylene diamine(t_R = 1.4 min),
(C) _N_-nitroso-_N_-methylethylamine(t_R = 3.0 min),
(D) malononitrile(t_R = 3.3 min),
(E) 2,6-diaminotoluene(t_R = 11.4 min),
(F) _p_-dinitrobenzene(t_R = 12.0 min), and
(G) _p_-nitroaniline(t_R = 14.3 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

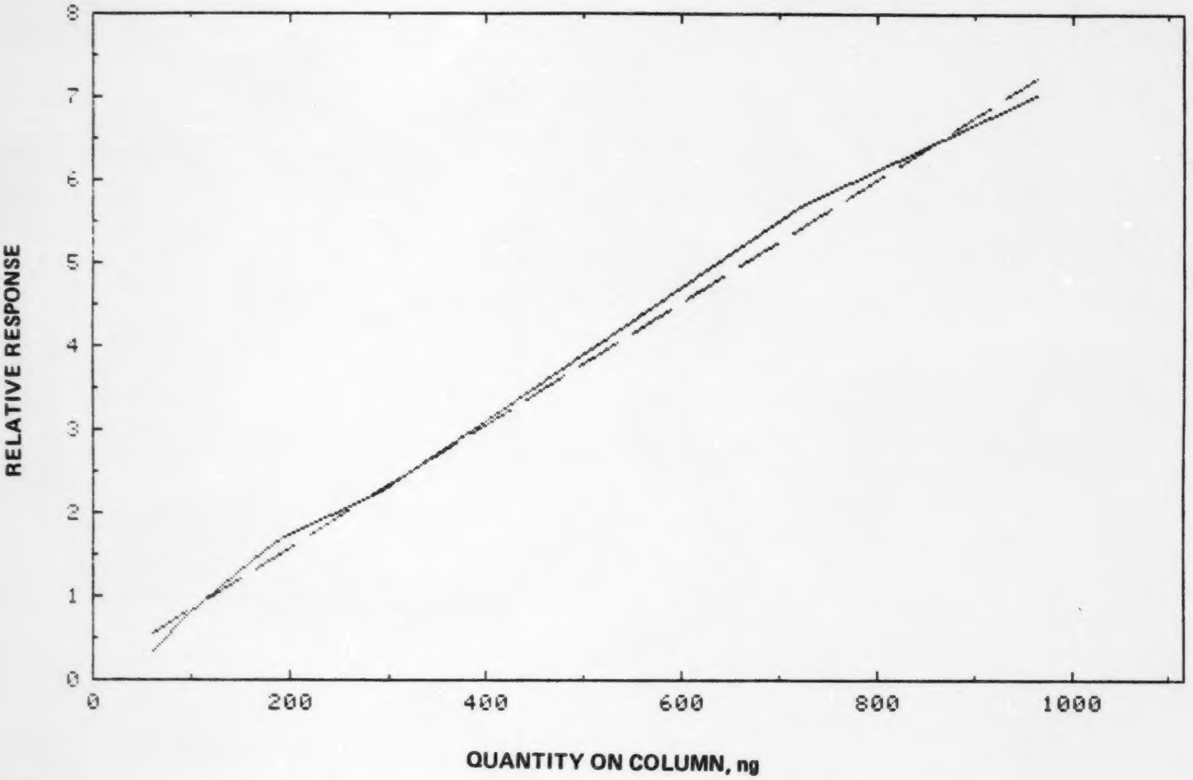

Figure A-16. Calibration curve for the determination of ethylene diamine by GC/FID.

Range: 97 - 970 ng
Correlation coefficient: 0.997
Slope: 7.4×10^{-3}
y-Intercept: 1.1×10^{-1}

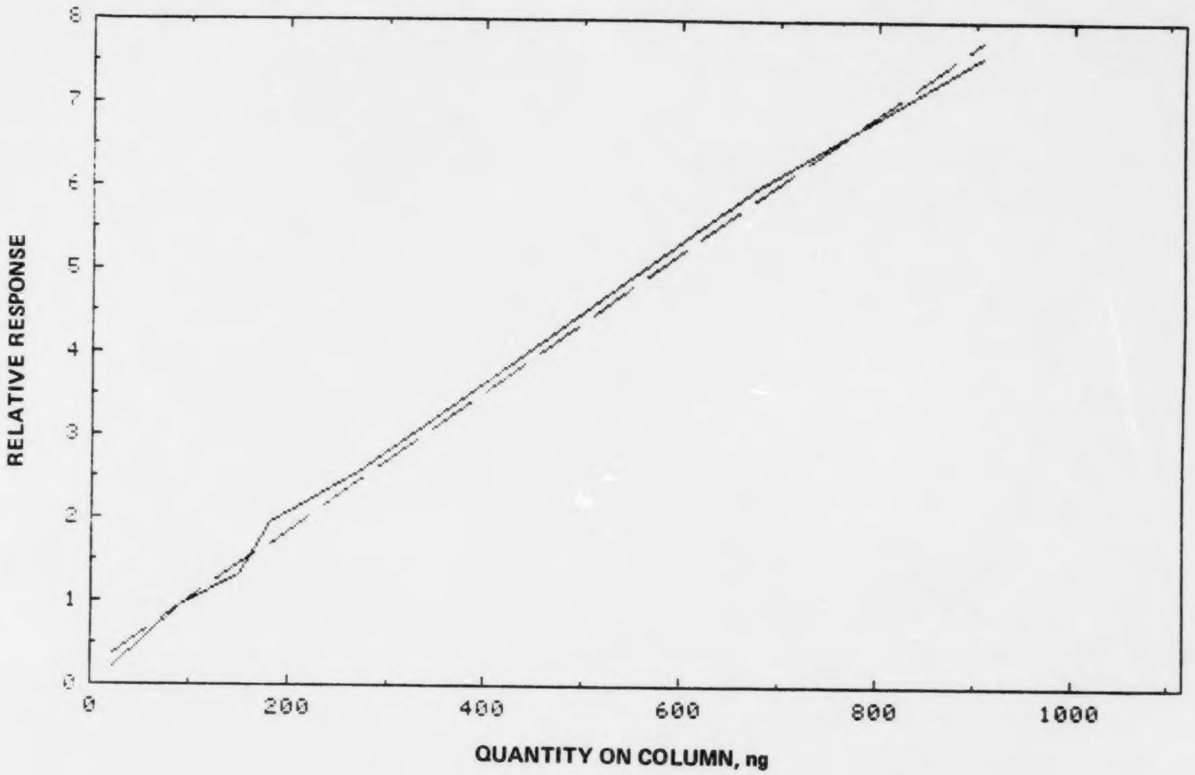

Figure A-17. Calibration curve for the determination of N-nitroso-N-methylethylamine by GC/FID.

Range: 57 - 910 ng
Correlation coefficient: 0.998
Slope: 8.5×10^{-3}
y-Intercept: 1.8×10^{-1}

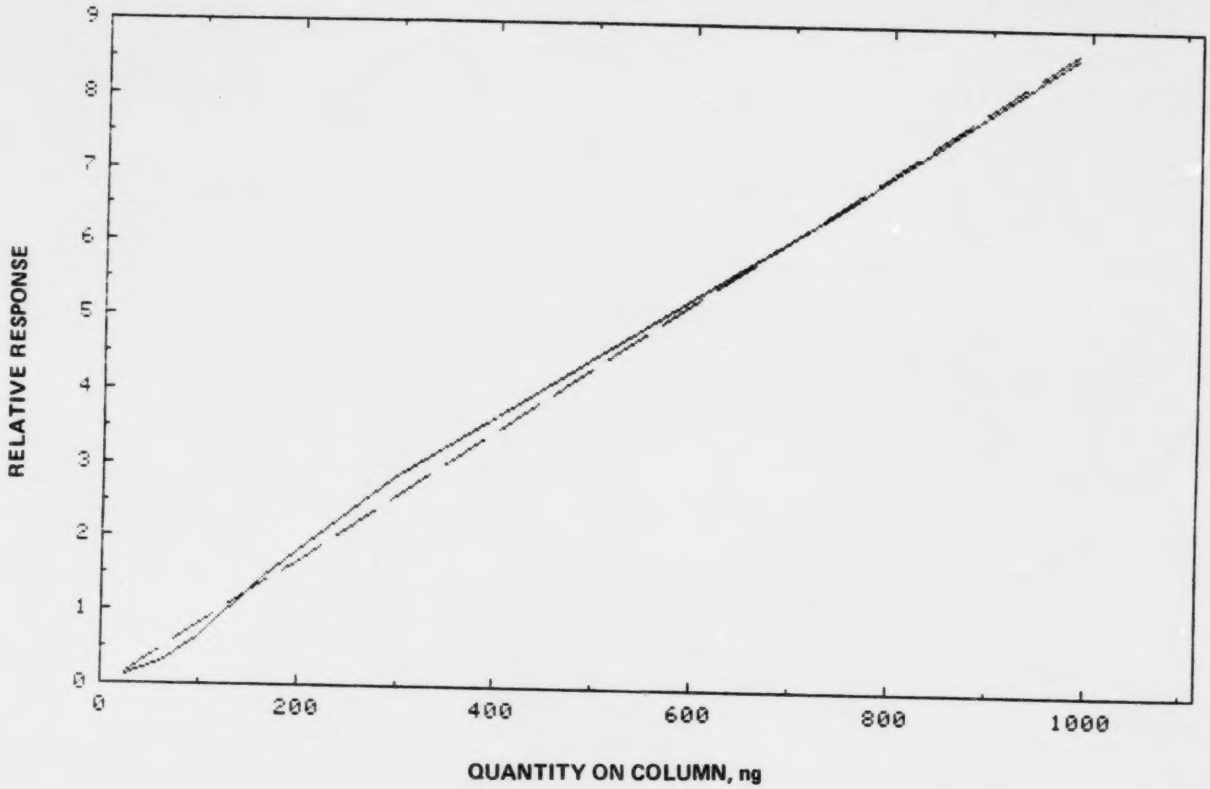

Figure A-18. Calibration curve for the determination of malononitrile by GC/FID.

Range: 99 - 990 ng
Correlation coefficient: 0.998
Slope: 8.9×10^{-3}
y-Intercept: -8.1×10^{-2}

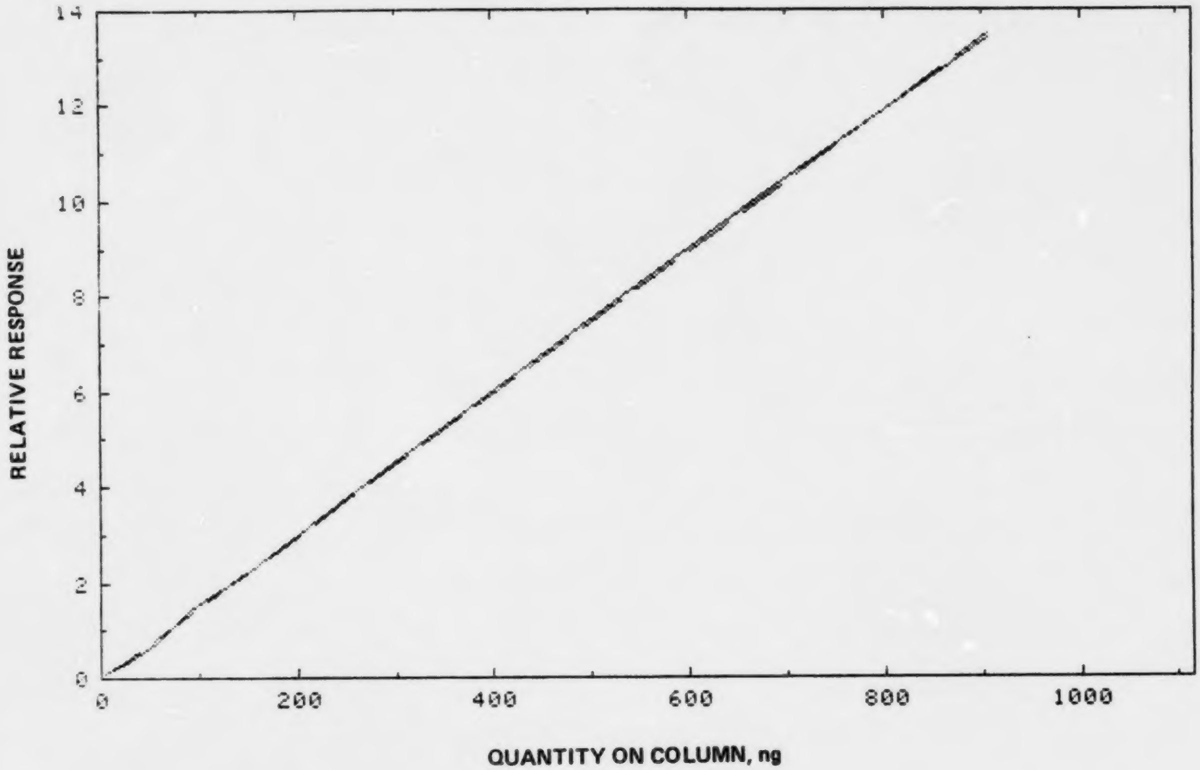

Figure A-19. Calibration curve for the determination of 2,6-diaminotoluene by GC/FID.

Range: 5.7 - 910 ng
Correlation coefficient: 0.999
Slope: 1.5×10^{-2}
y-Intercept: -1.0×10^{-2}

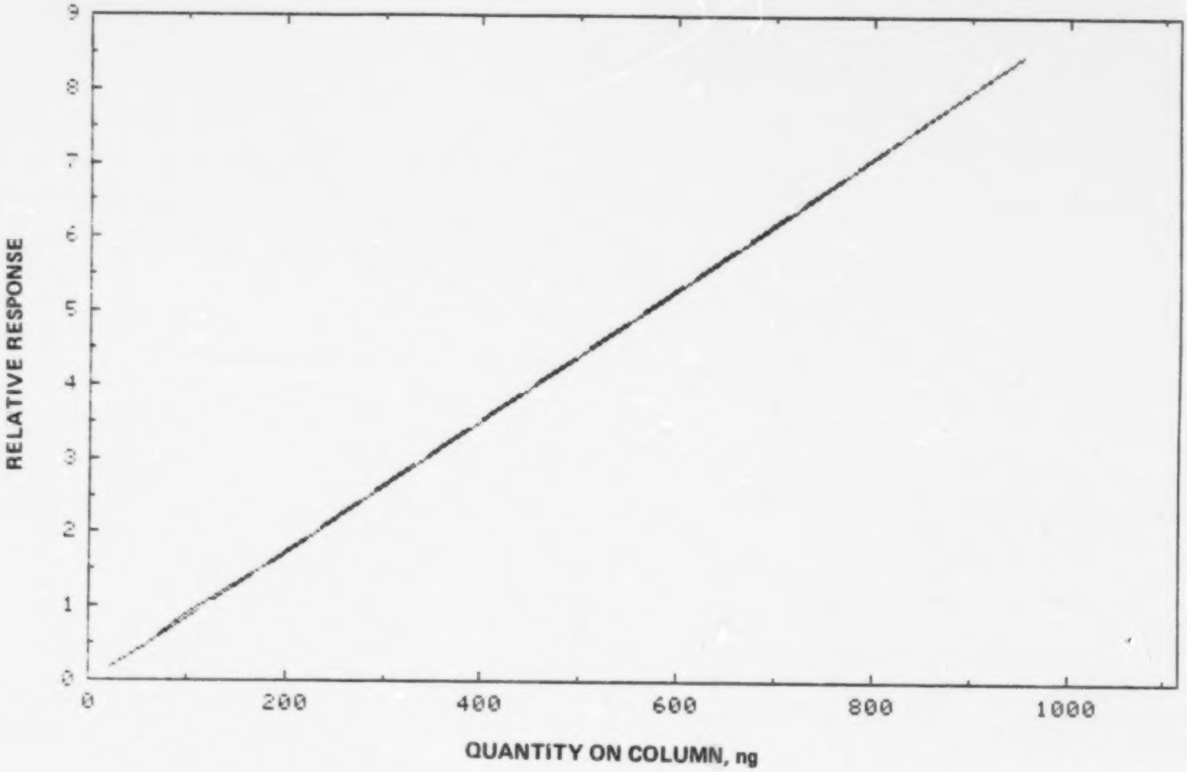

Figure A-20. Calibration curve for the determination of p-dinitrobenzene by GC/FID.

Range: 24 - 950 ng
Correlation coefficient: 0.999
Slope: 8.9×10^{-3}
y-Intercept: -4.4×10^{-2}

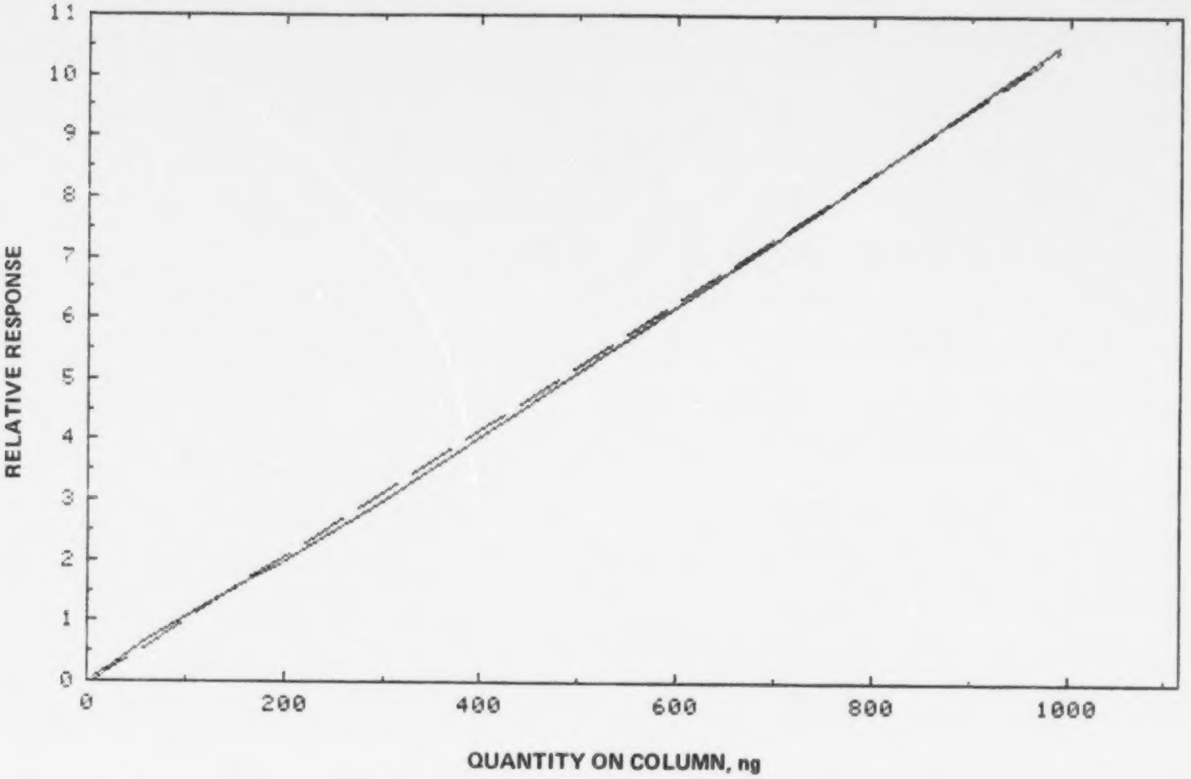

Figure A-21. Calibration curve for the determination of p-nitroaniline by GC/FID.

Range: 6.0 - 990 ng
Correlation coefficient: 0.999
Slope: 1.1×10^{-2}
y-Intercept: -5.9×10^{-2}

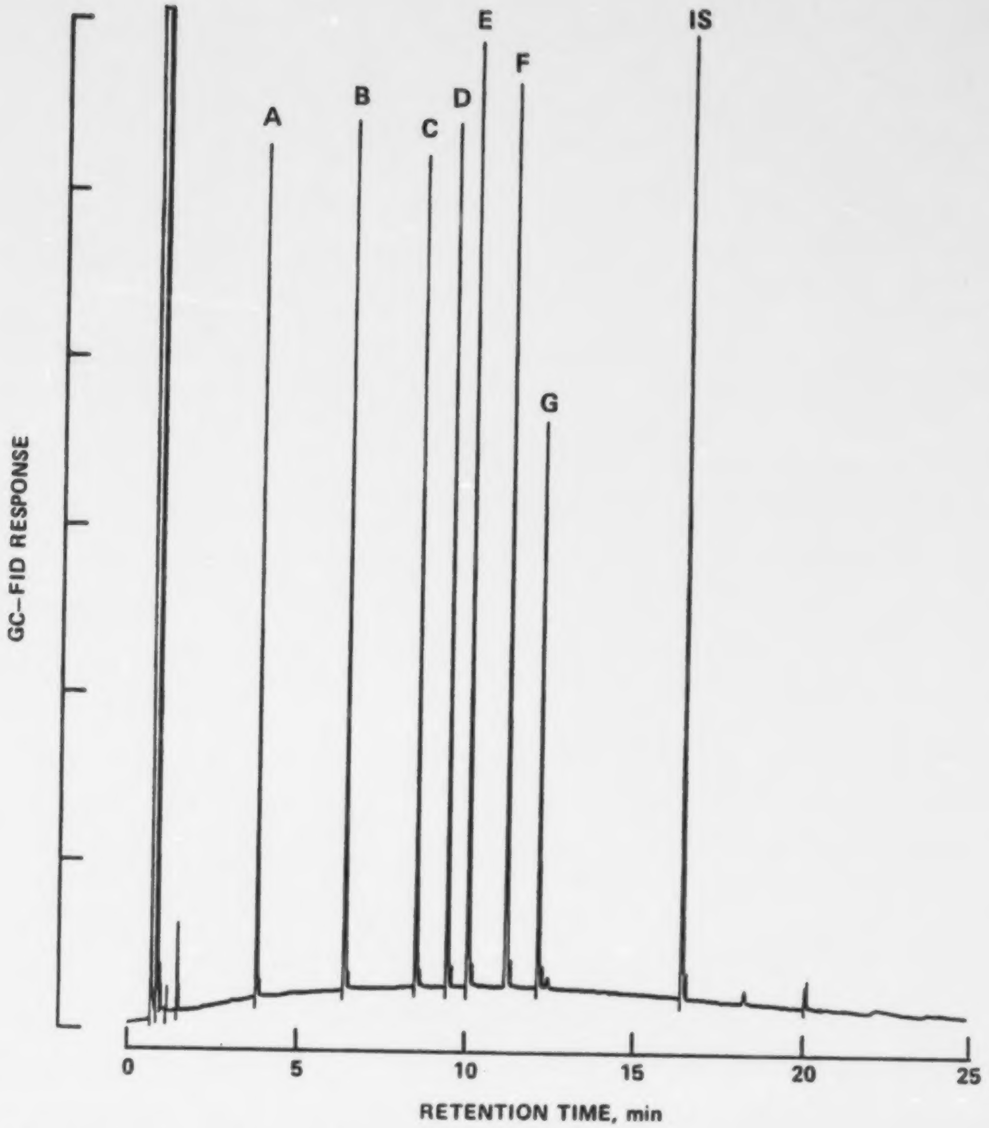

Figure A-22. Chromatogram by GC/FID for

(A) N-nitrosodiethylamine(t_R = 3.9 min),
(B) N-nitrosopyrrolidine(t_R = 6.8 min),
(C) 4-chloroaniline(t_R = 8.8 min),
(D) N-nitrosodibutylamine(t_R = 9.7 min),
(E) 3,4-diaminotoluene(t_R = 10.4 min),
(F) 2,4-diaminotoluene(t_R = 11.6 min), and
(G) m-dinitrobenzene(t_R = 12.4 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

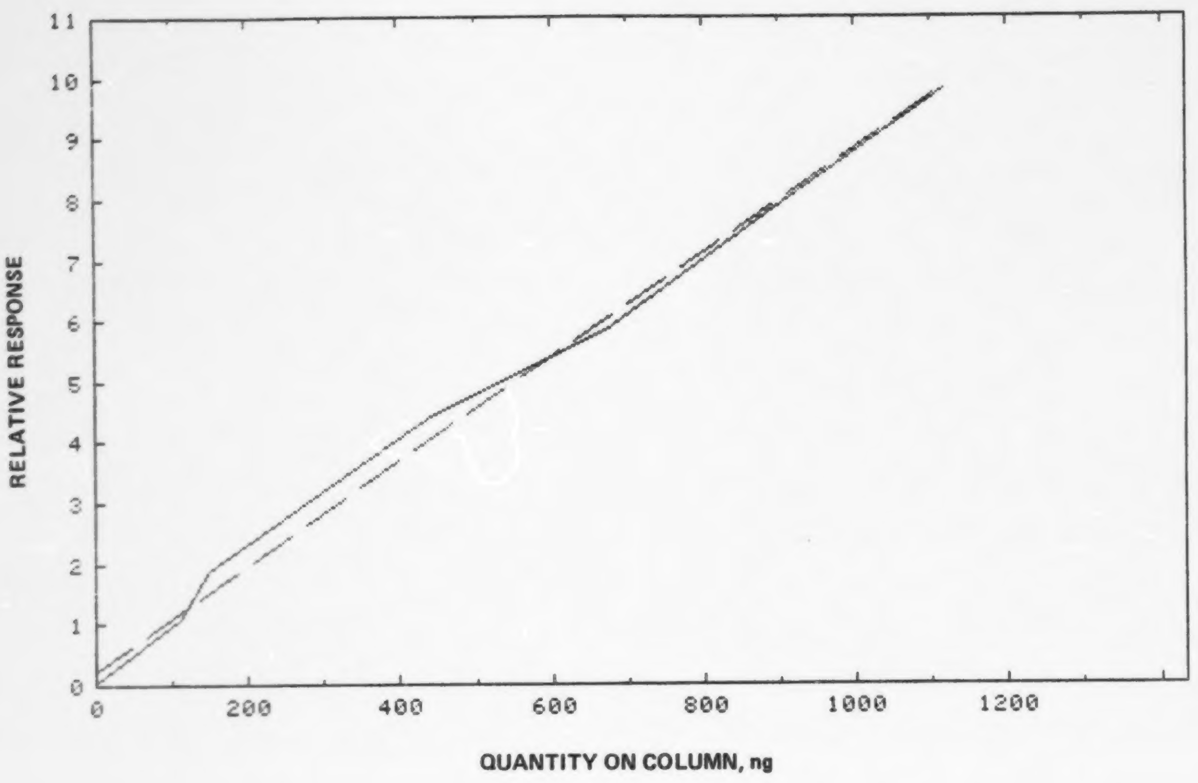

Figure A-23. Calibration curve for the determination of N-nitrosodiethylamine by GC/FID.

Range: 110 - 1100 ng
Correlation coefficient: 0.997
Slope: 8.6×10^{-3}
y-Intercept: 2.4×10^{-1}

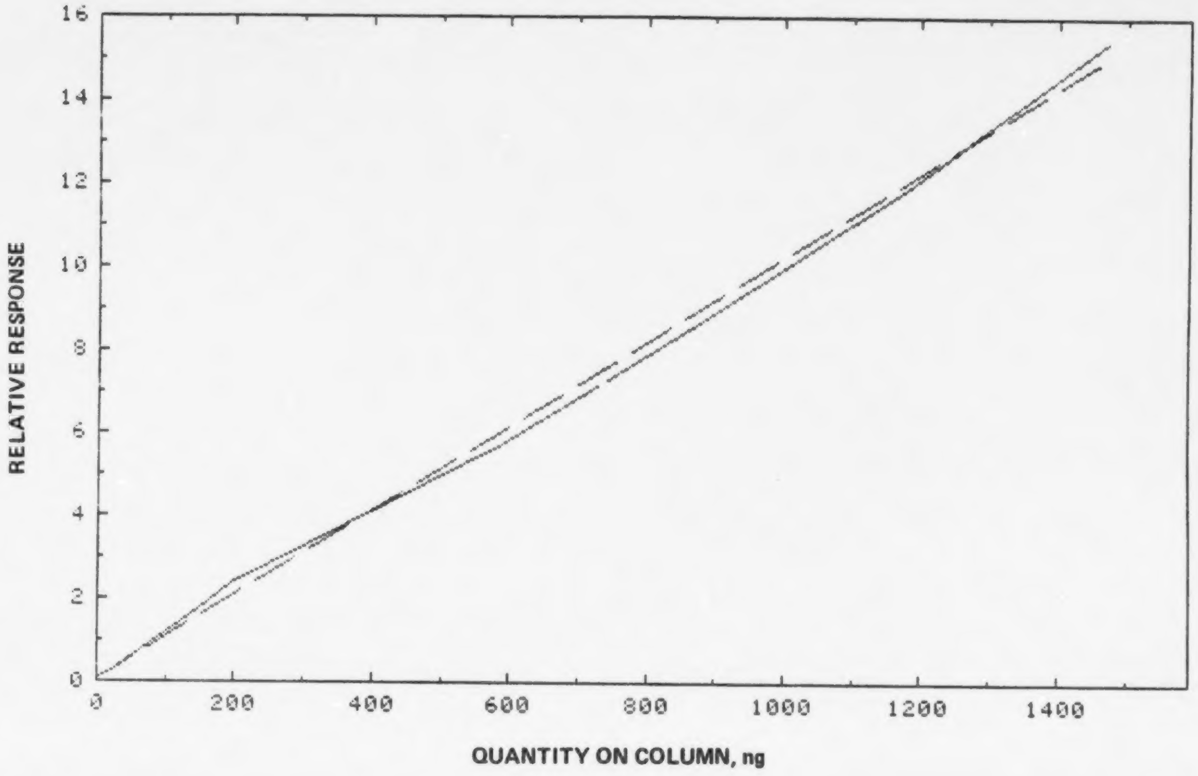

Figure A-24. Calibration curve for the determination of N-nitrosopyrrolidine by GC/FID.

Range: 15 - 1500 ng
Correlation coefficient: 0.998
Slope: 1.0×10^{-2}
y-Intercept: 7.6×10^{-2}

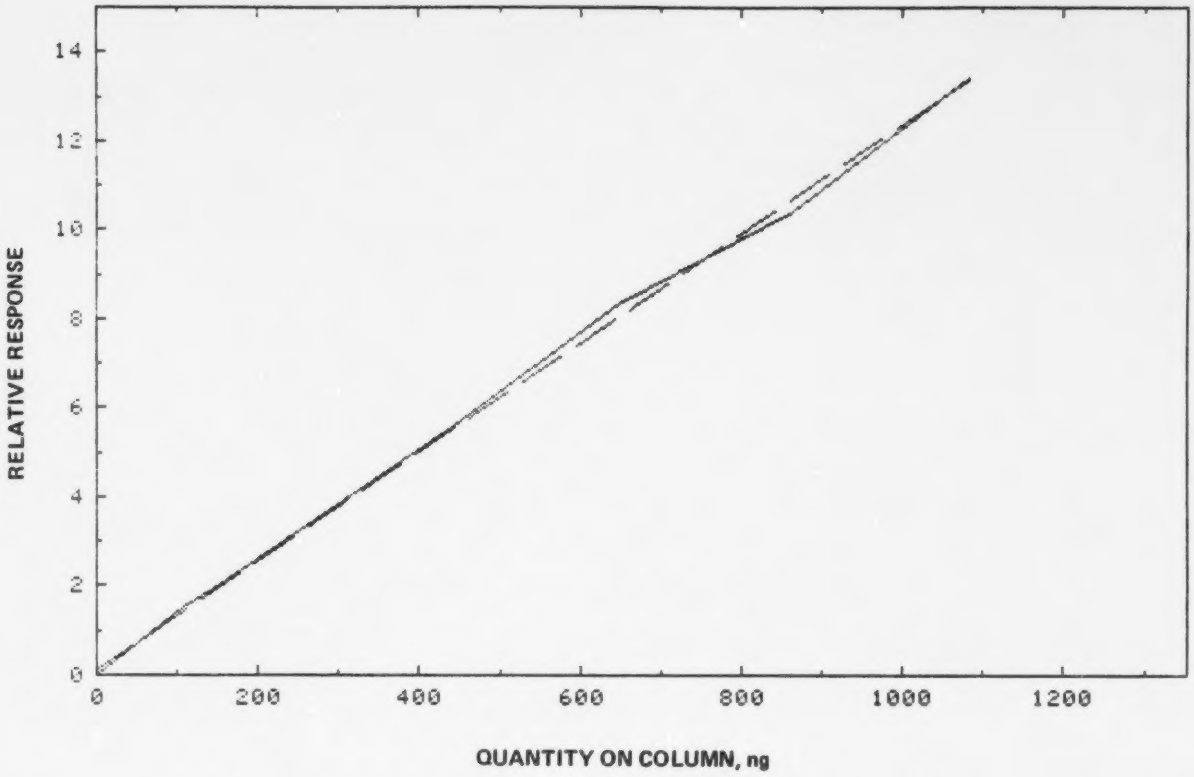

Figure A-25. Calibration curve for the determination of 4-chloroaniline by GC/FID.

Range: 11 - 1100 ng
Correlation coefficient: 0.999
Slope: 1.2×10^{-2}
y-Intercept: 1.3×10^{-1}

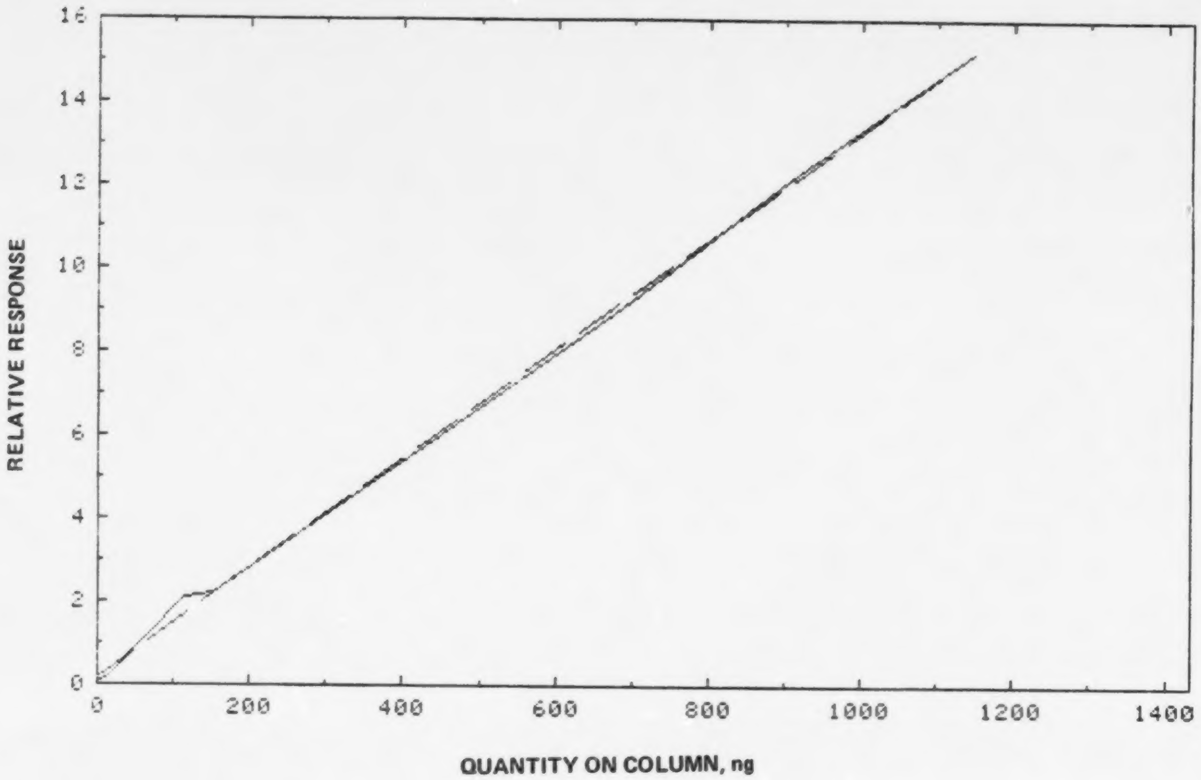

Figure A-26. Calibration curve for the determination of N-nitrosodibutylamine by GC/FID.

Range: 110 - 1100 ng
Correlation coefficient: 0.999
Slope: 1.3×10^{-2}
y-Intercept: 1.9×10^{-1}

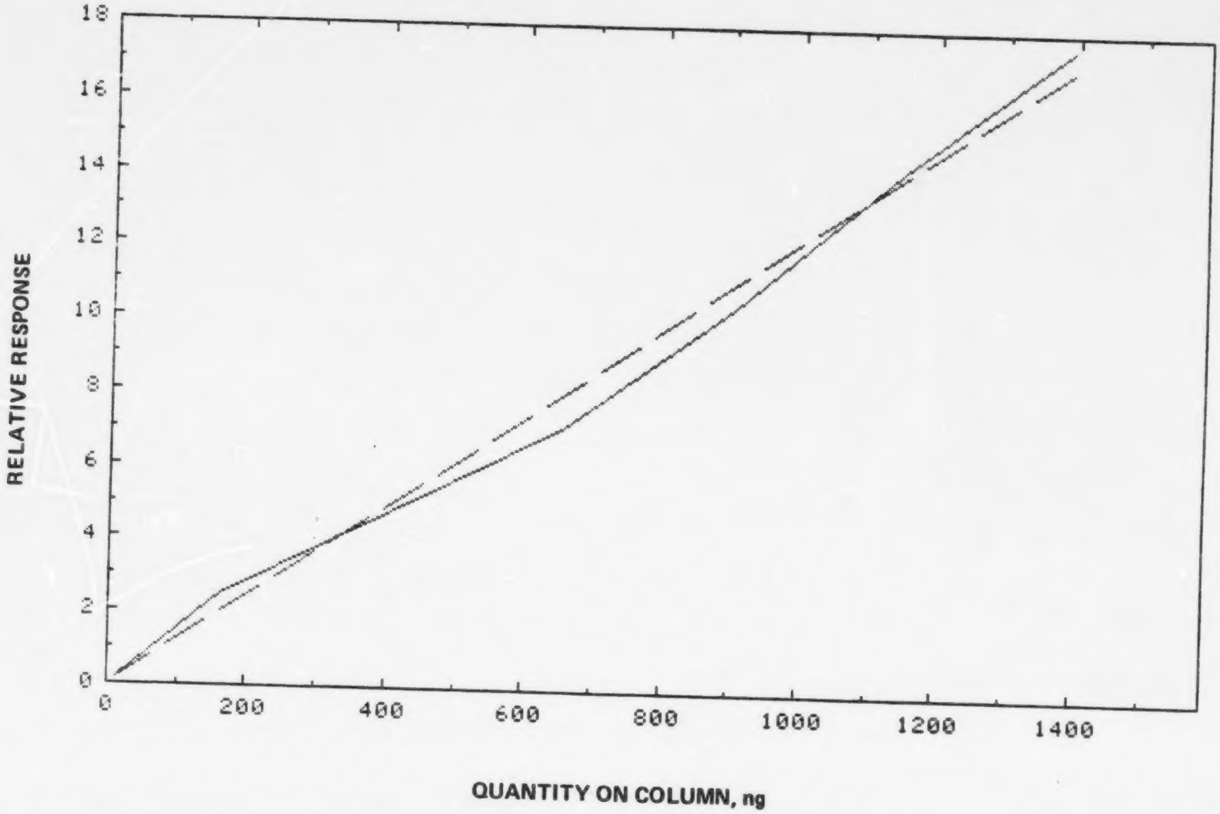

Figure A-27. Calibration curve for the determination of 3,4-diaminotoluene by GC/FID.

Range: 12 - 1400 ng
Correlation coefficient: 0.996
Slope: 1.2×10^{-2}
y-Intercept: 2.0×10^{-2}

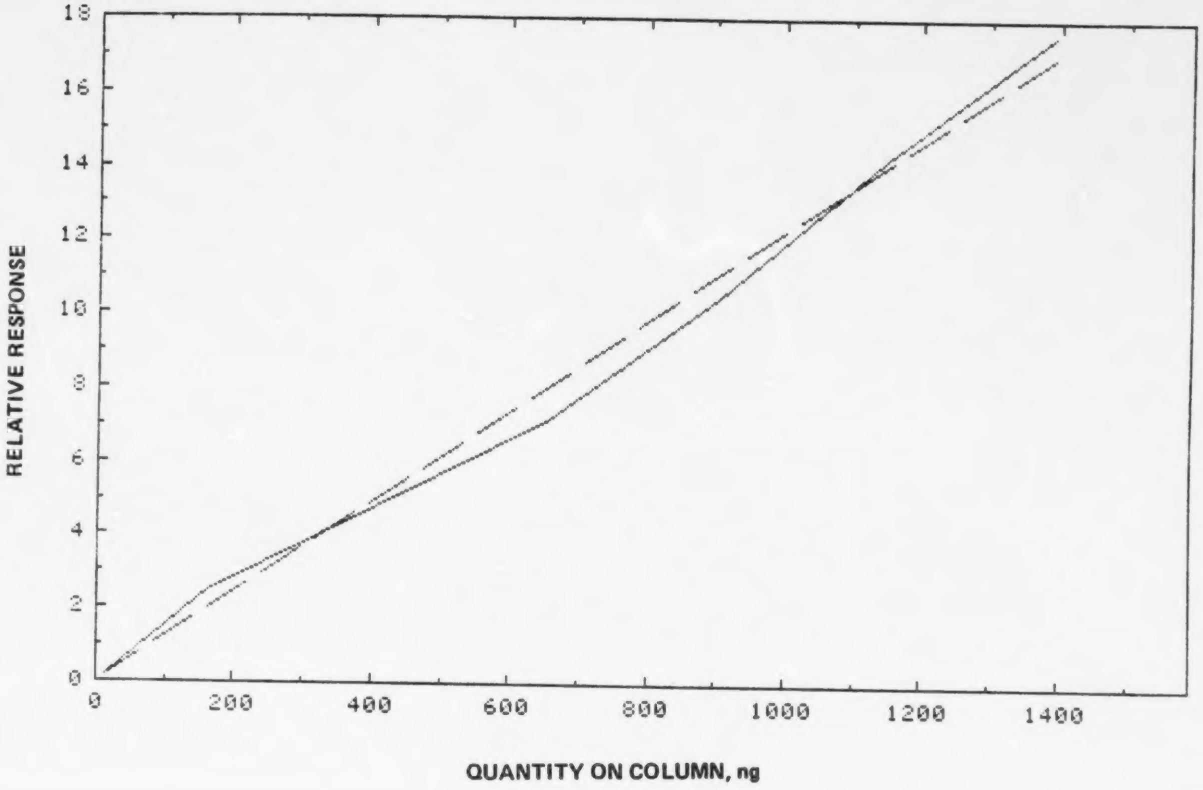

Figure A-28. Calibration curve for the determination of 2,4-diaminotoluene by GC/FID.

Range: 12 - 1400 ng
Correlation coefficient: 0.996
Slope: 1.2×10^{-2}
y-Intercept: 5.0×10^{-2}

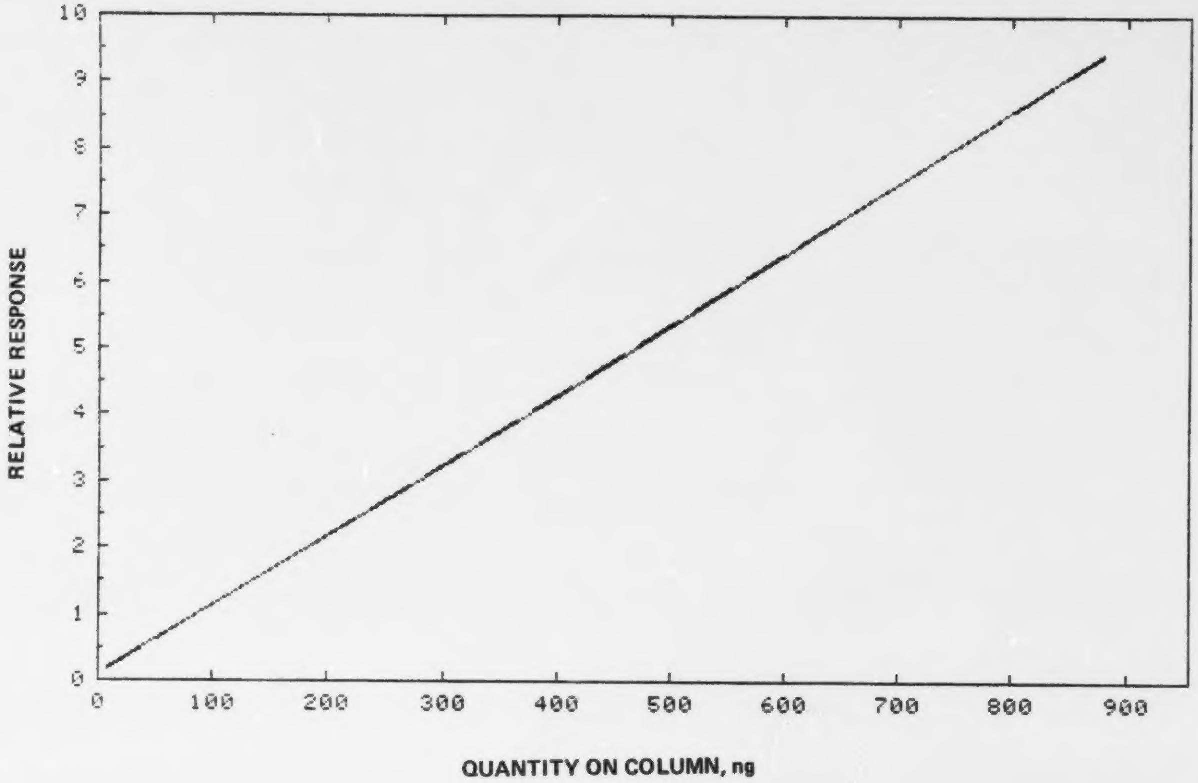

Figure A-29. Calibration curve for the determination of m-dinitrobenzene by GC/FID.

Range: 120 - 880 ng
Correlation coefficient: 0.999
Slope: 1.1×10^{-2}
y-Intercept: 6.1×10^{-2}

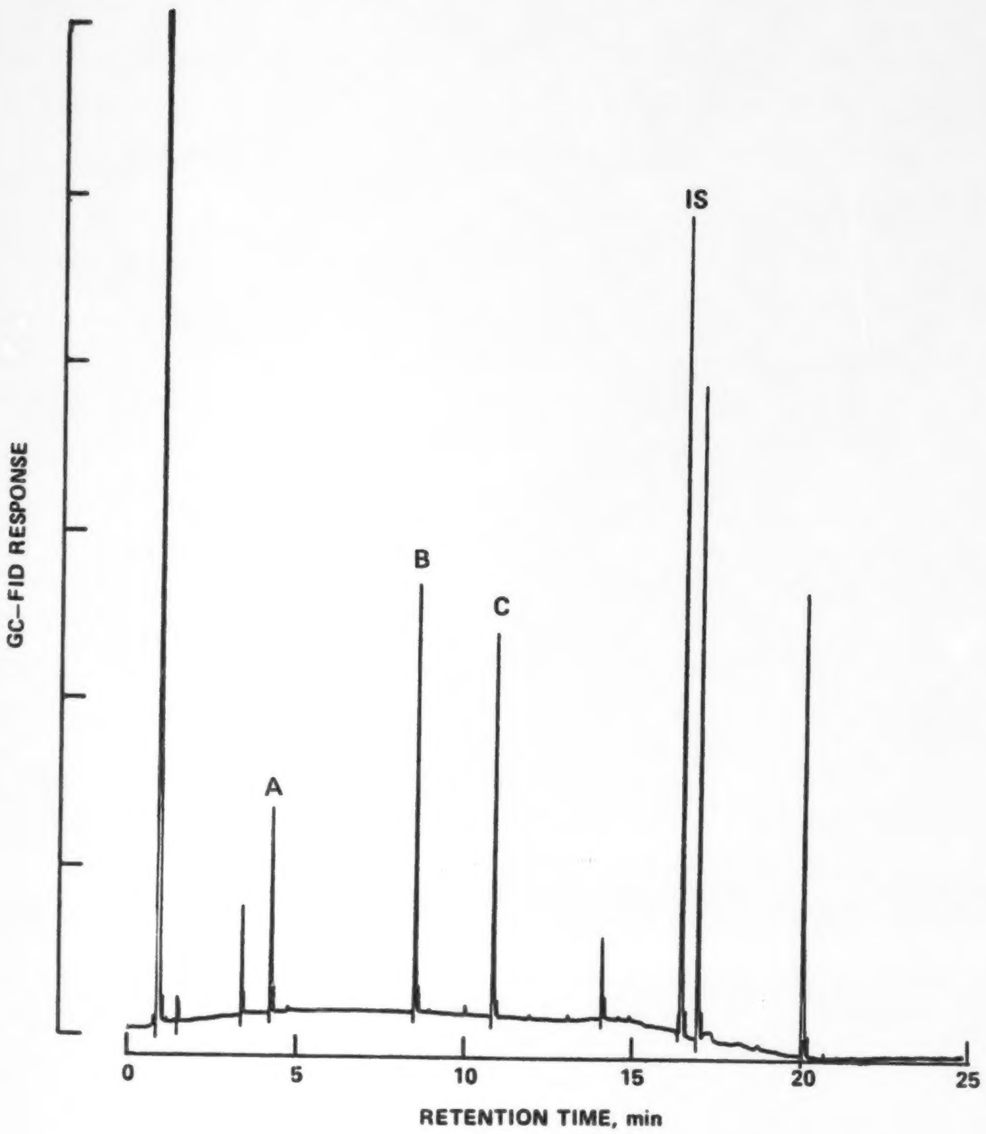

Figure A-30. Chromatogram by GC/FID for

(A) N-nitroso-N-methylurethane(t_R = 4.4 min),
(B) 2,6-dichlorophenol(t_R = 8.7 min), and
(C) 2,4,5-trichlorophenol(t_R = 11.0 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

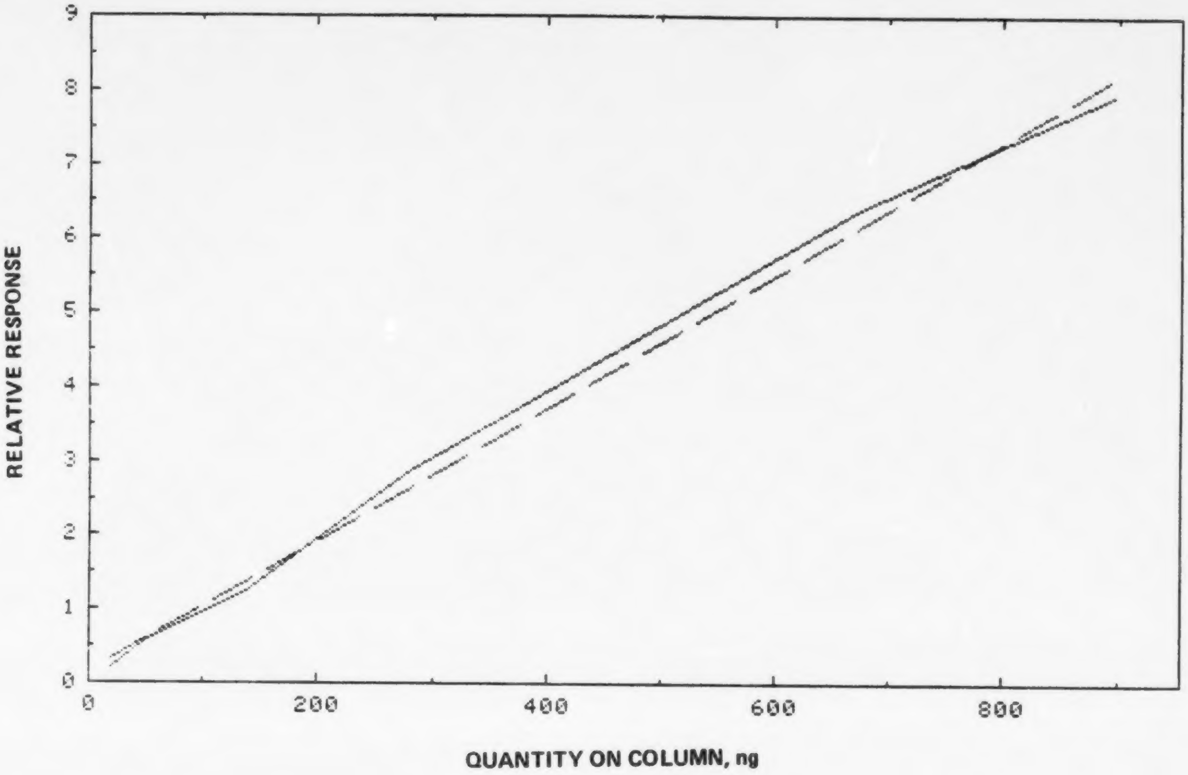

Figure A-31. Calibration curve for the determination of 2,6-dichlorophenol by GC/FID.

Range: 20 - 900 ng
Correlation coefficient: 0.998
Slope: 8.9×10^{-3}
y-Intercept: 1.4×10^{-1}

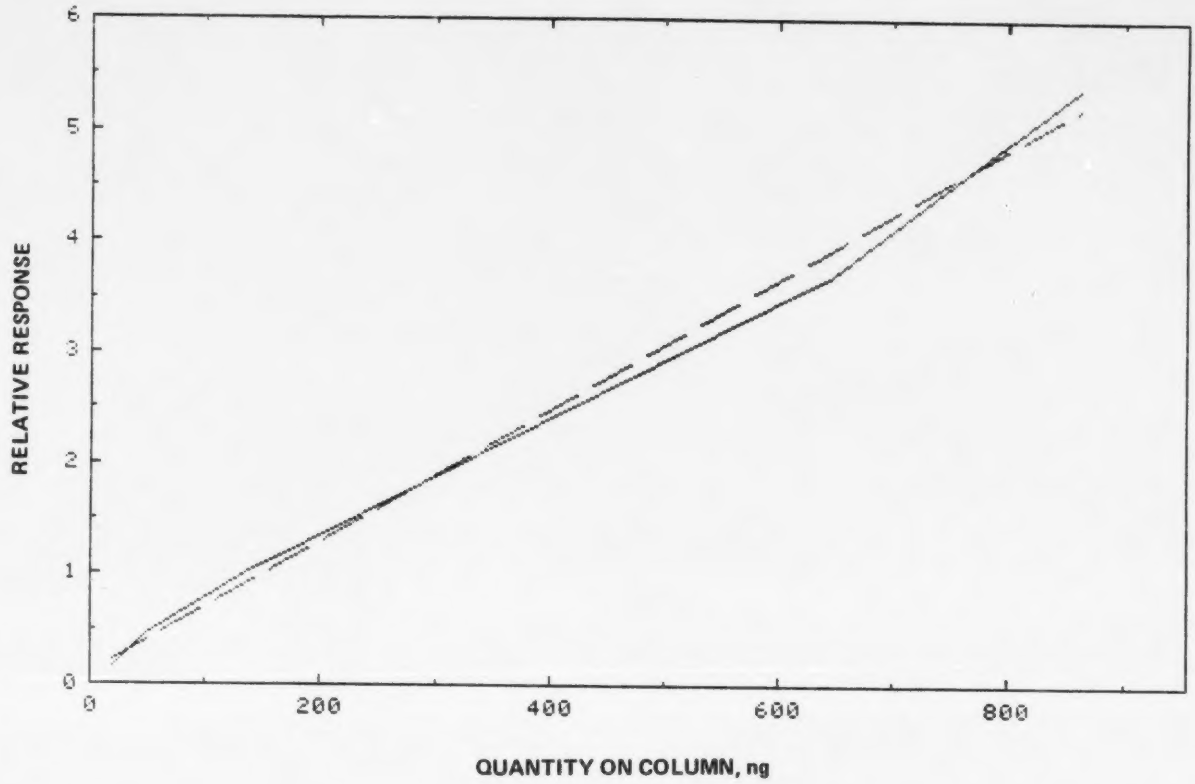

Figure A-32. Calibration curve for the determination of 2,4,5-trichlorophenol by GC/FID.

Range: 20 - 860 ng
Correlation coefficient: 0.998
Slope: 5.9×10^{-3}
y-Intercept: 1.1×10^{-1}

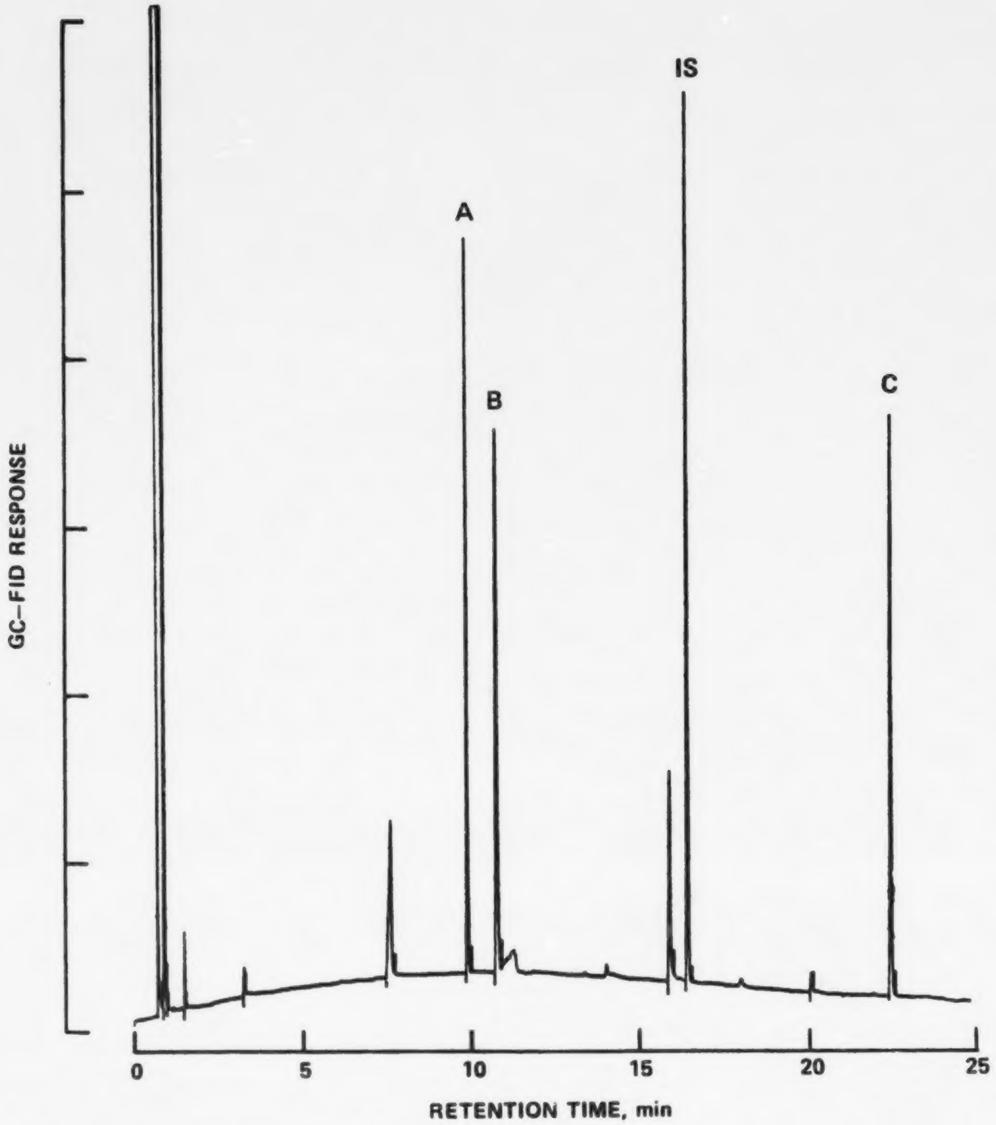

Figure A-33. Chromatogram by GC/FID for

(A) safrole(t_R = 9.9 min),
(B) nicotine(t_R = 10.7 min), and
(C) 2-acetamidofluorene(t_R = 22.5 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

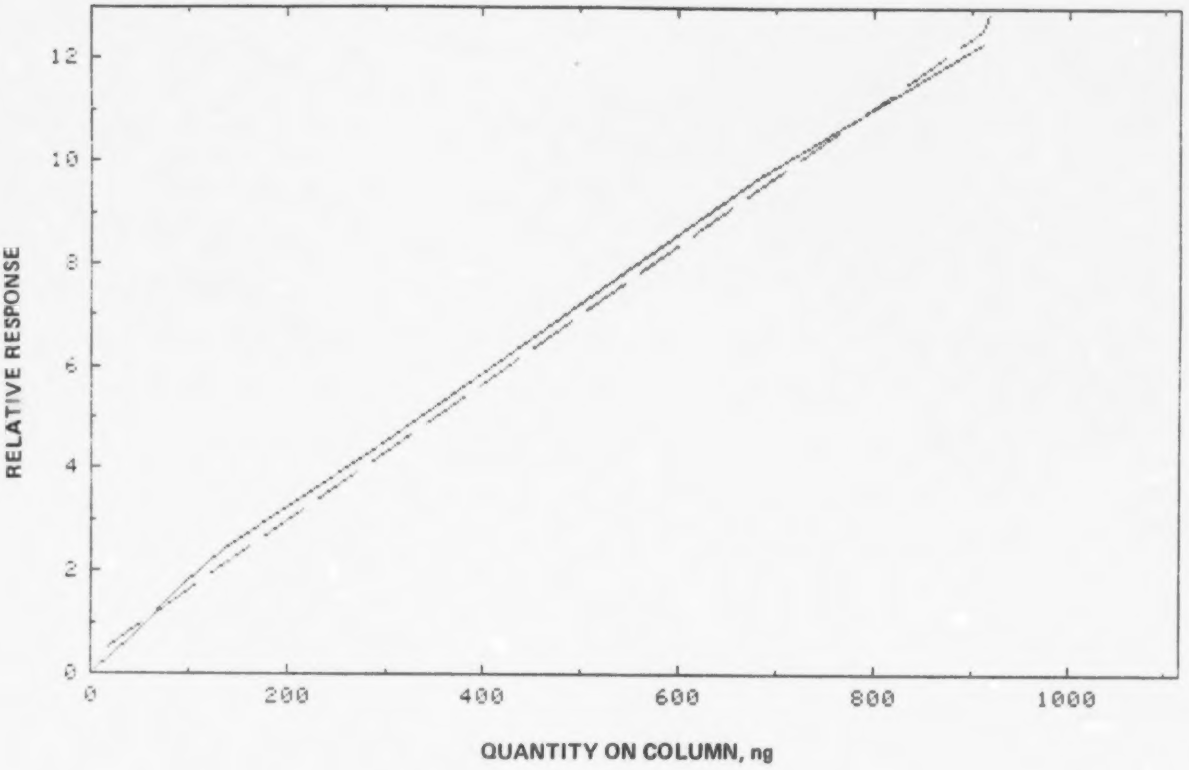

Figure A-34. Calibration curve for the determination of safrole by GC/FID.

Range: 46 - 910 ng
Correlation coefficient: 0.999
Slope: 1.4×10^{-2}
y-Intercept: 2.8×10^{-1}

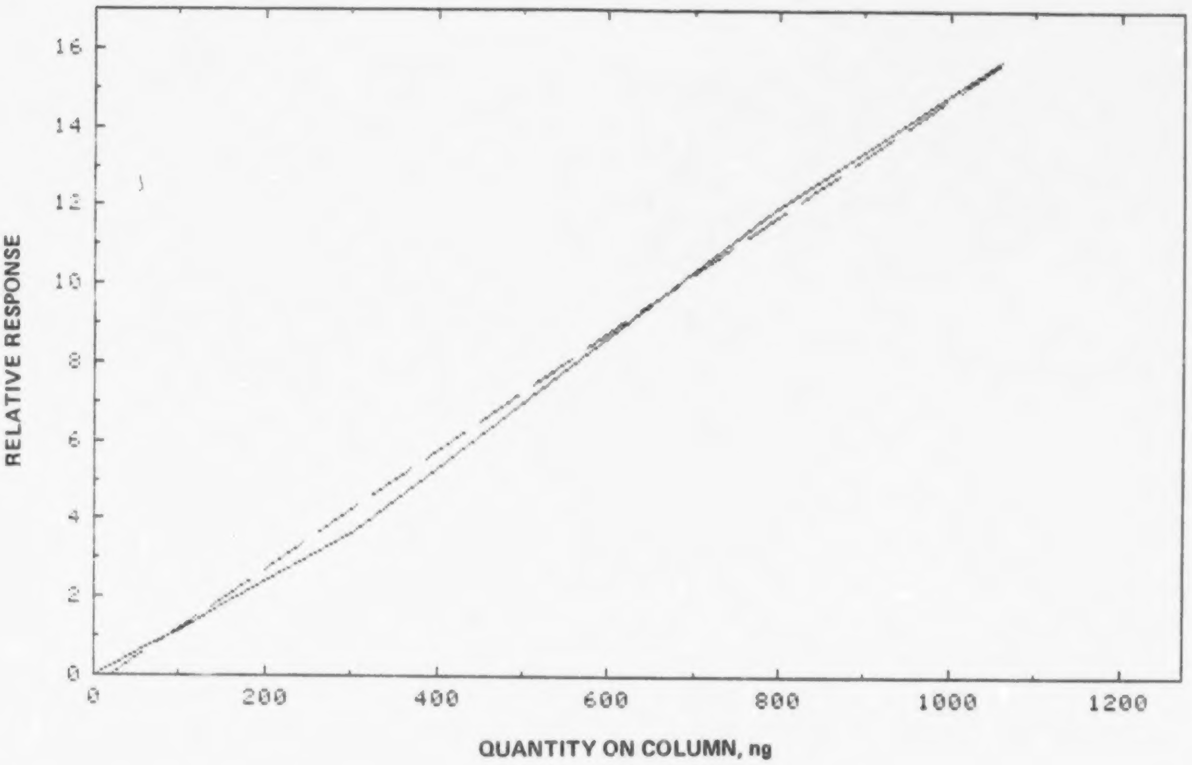

Figure A-35. Calibration curve for the determination of nicotine by GC/FID.

Range: 53 - 1100 ng
Correlation coefficient: 0.998
Slope: 1.5 x 10^{-2}
y-Intercept: -3.1 x 10^{-1}

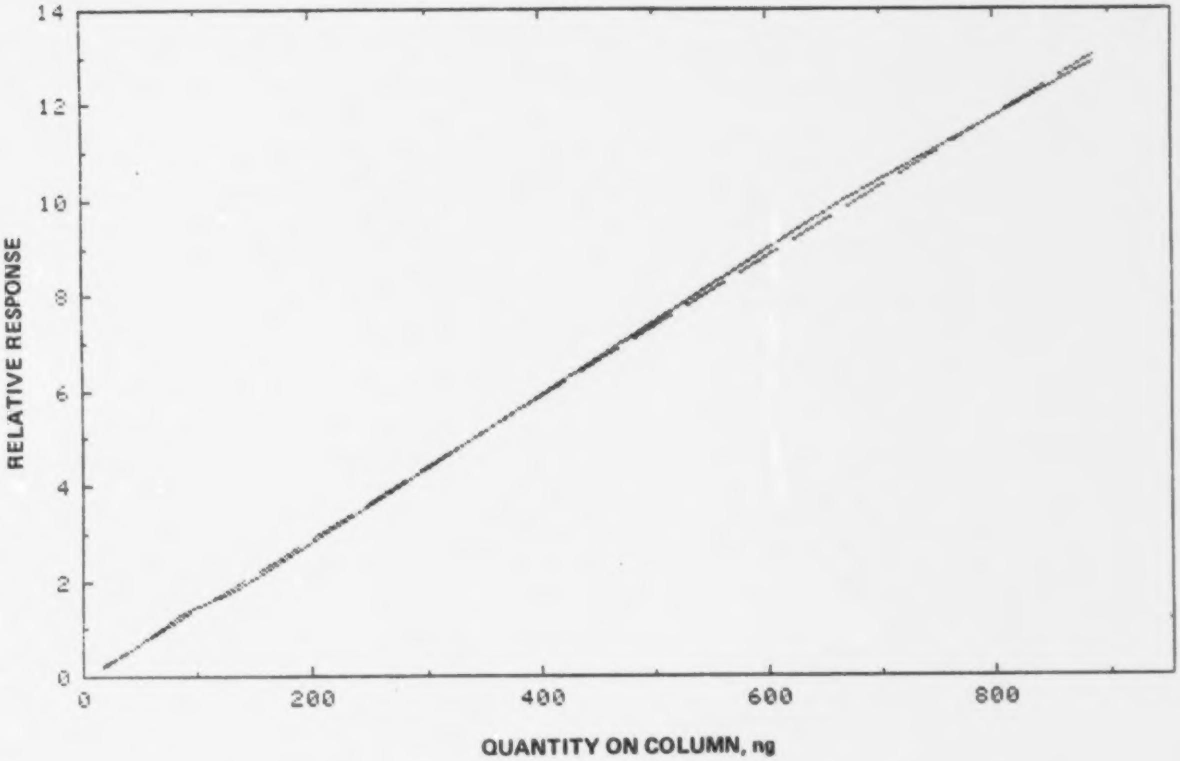

Figure A-36. Calibration curve for the determination of 2-acetamidofluorene by GC/FID.

Range: 18 - 890 ng
Correlation coefficient: 0.999
Slope: 1.5 x 10^{-2}
y-Intercept: -5.3 x 10^{-2}

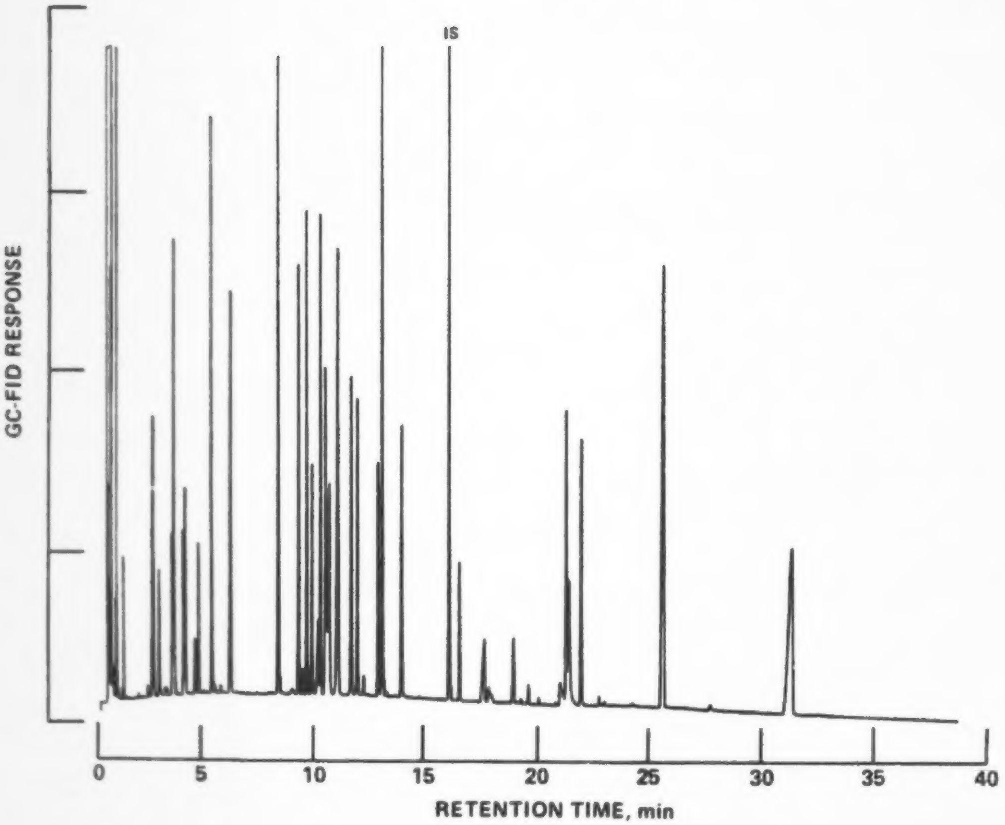

Figure A-37. Chromatogram by GC/FID for all candidate POHCs.

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

APPENDIX B

CHROMATOGRAMS, MASS SPECTRA, AND CALIBRATION CURVES FOR GC/MS DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference mass spectrum Figure No.	Reference calibration curve Figure No.
2-Acetamidofluorene	B-58	B-63	--[a]
Benzyl chloride	B-1	B-6	B-7
4-Chloroaniline	B-26	B-31	B-32
2,4-Diaminotoluene	B-26	B-37	B-38
2,6-Diaminotoluene	B-41	B-44	B-45
3,4-Diaminotoluene	B-26	B-35	B-36
Dibenz[a,j]acridine	B-12	B-19	B-20
2,6-Dichlorophenol	B-51	B-54	B-55
1,3-Dichloro-2-propanol	B-1	B-2	B-3
9,10-Dimethyl-1,2-benzanthracene	B-12	B-17	B-18
Dimethyl sulfate	B-12	B-13	B-14
m-Dinitrobenzene	B-26	B-39	B-40
p-Dinitrobenzene	B-41	B-46	B-47
Malononitrile	B-41	B-50	--[a]
Methanesulfonic acid ethyl ester	B-21	B-22	B-23
1,4-Naphthoquinone	B-12	B-15	B-16
alpha-Naphthylamine	B-21	B-24	B-25
Nicotine	B-58	B-61	B-62
p-Nitroaniline	B-41	B-48	B-49
N-Nitrosodibutylamine	B-26	B-33	B-34
N-Nitrosodiethylamine	B-26	B-27	B-28
N-Nitroso-*N*-methylethylamine	B-41	B-42	B-43
N-Nitrosopyrrolidine	B-26	B-29	B-30
Pentachlorobenzene	B-1	B-10	B-11
Pentachloroethane	B-1	B-4	B-5
Safrole	B-58	B-59	B-60
1,2,4,5-Tetrachlorobenzene	B-1	B-8	B-9
2,4,5-Trichlorophenol	B-51	B-56	B-57

[a] Calibration curve not available.

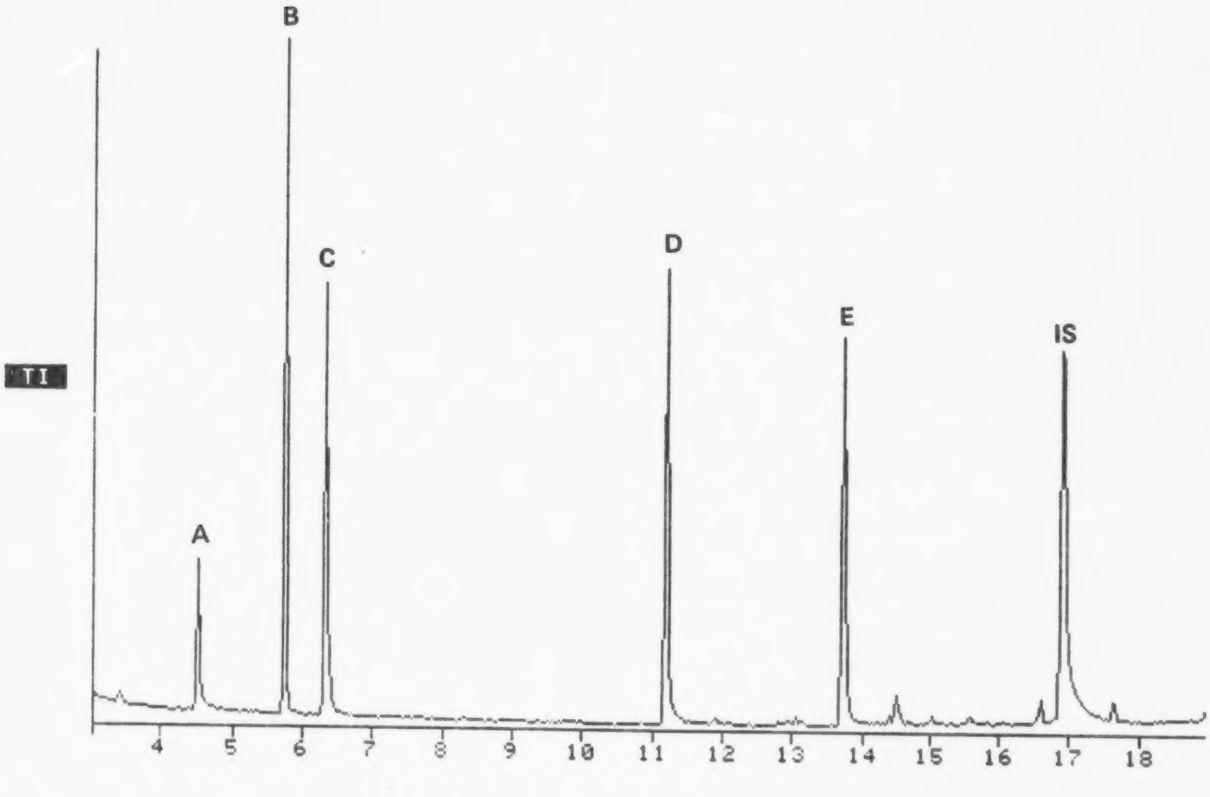

Figure B-1. Chromatogram by GC/MS for

(A) 1,3-dichloro-2-propanol(t_R = 4.6 min).
(B) pentachloroethane(t_R = 5.7 min),
(C) benzyl chloride(t_R = 6.4 min),
(D) 1,2,4,5-tetrachlorobenzene(t_R = 11.2 min), and
(E) pentachlorobenzene(t_R = 13.8 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

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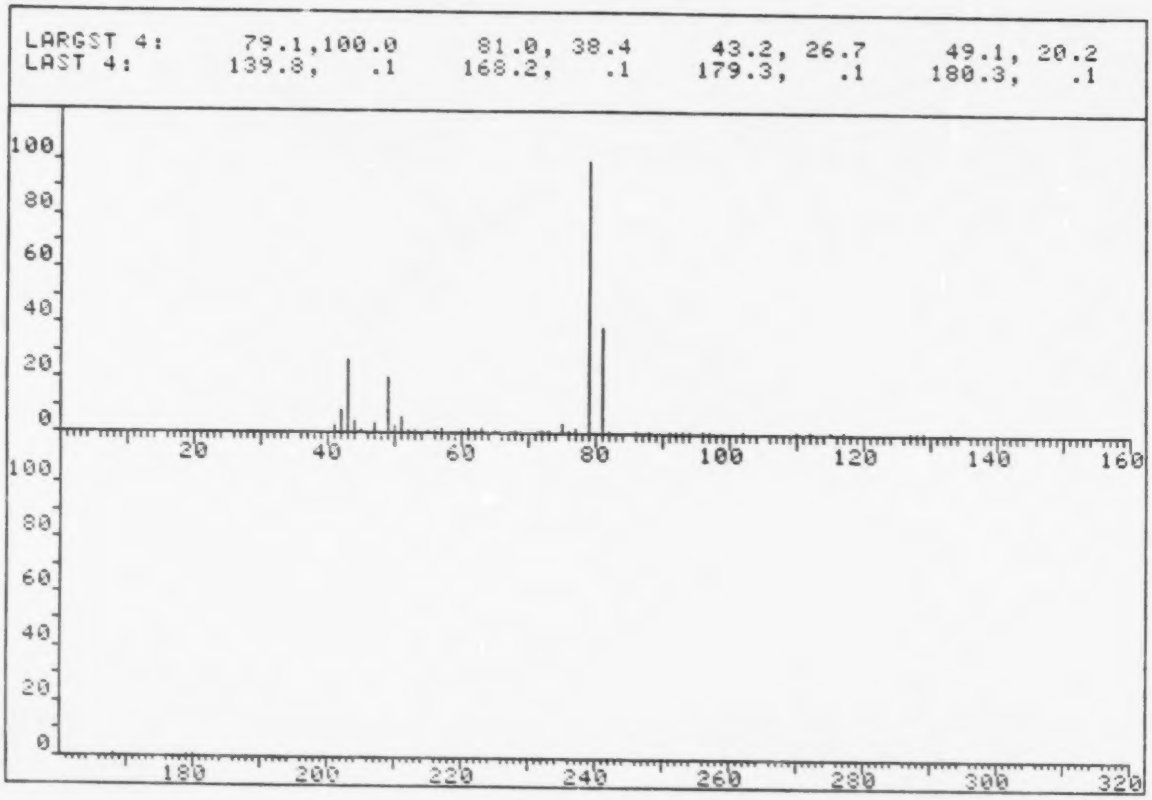


Figure B-2. Mass spectrum for 1,3-dichloro-2-propanol.

TABLE B.1 KEY IONS AND RELATIVE ABUNDANCES FOR 1,3-DICHLORO-2-PROPANOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	2.3	77	1.8	168	.1
42	8.1	79	100.0		
43	26.7	81	38.4	179	.1
44	4.1	82	.7	180	.1
45	.6	86	.4		
47	3.5	88	.2		
49	20.2	91	1.1		
50	2.5	92	.4		
51	5.9	93	.5		
52	1.0	94	.4		
53	.9	96	.2		
55	1.2	97	.2		
56	.7	102	.2		
57	1.5				
60	.7	110	.2		
61	1.6	112	.1		
		115	.0		
62	.7	117	.1		
63	1.7				
65	1.0	127	.1		
68	.1	128	.1		
72	.5	129	.2		
73	1.1				
75	3.8	133	.1		
		140	.1		
76	1.2				

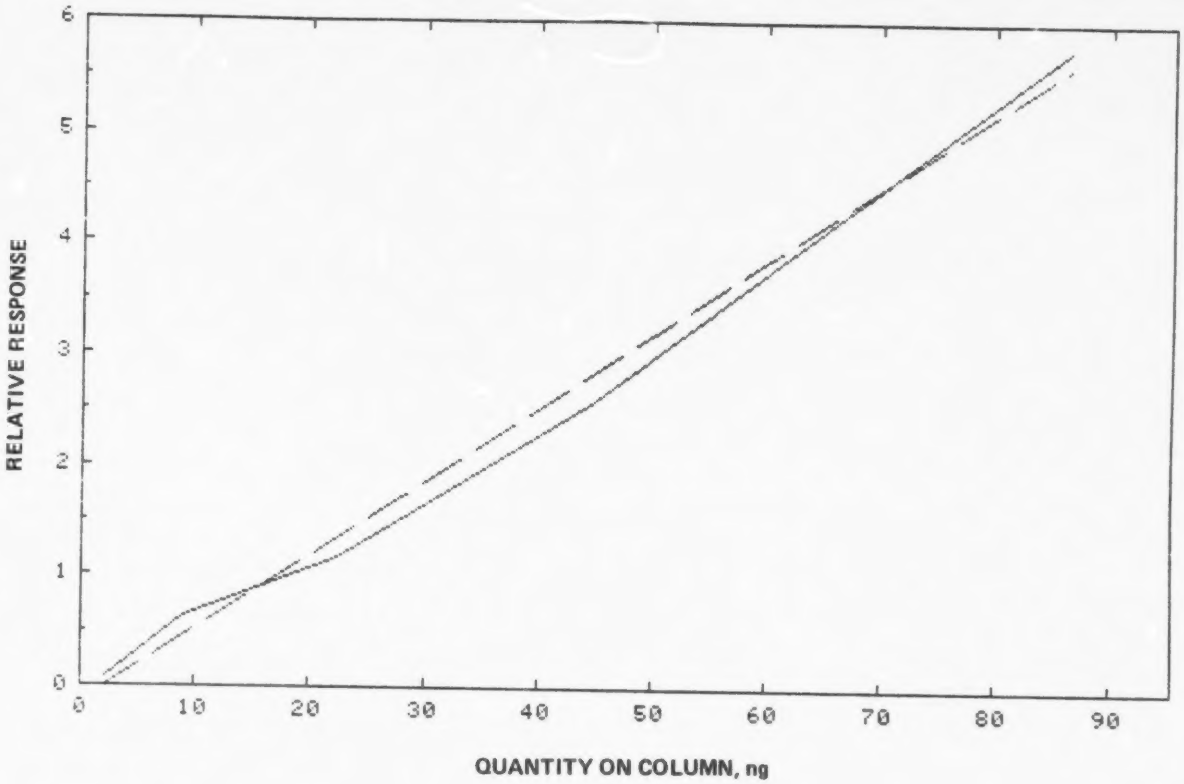
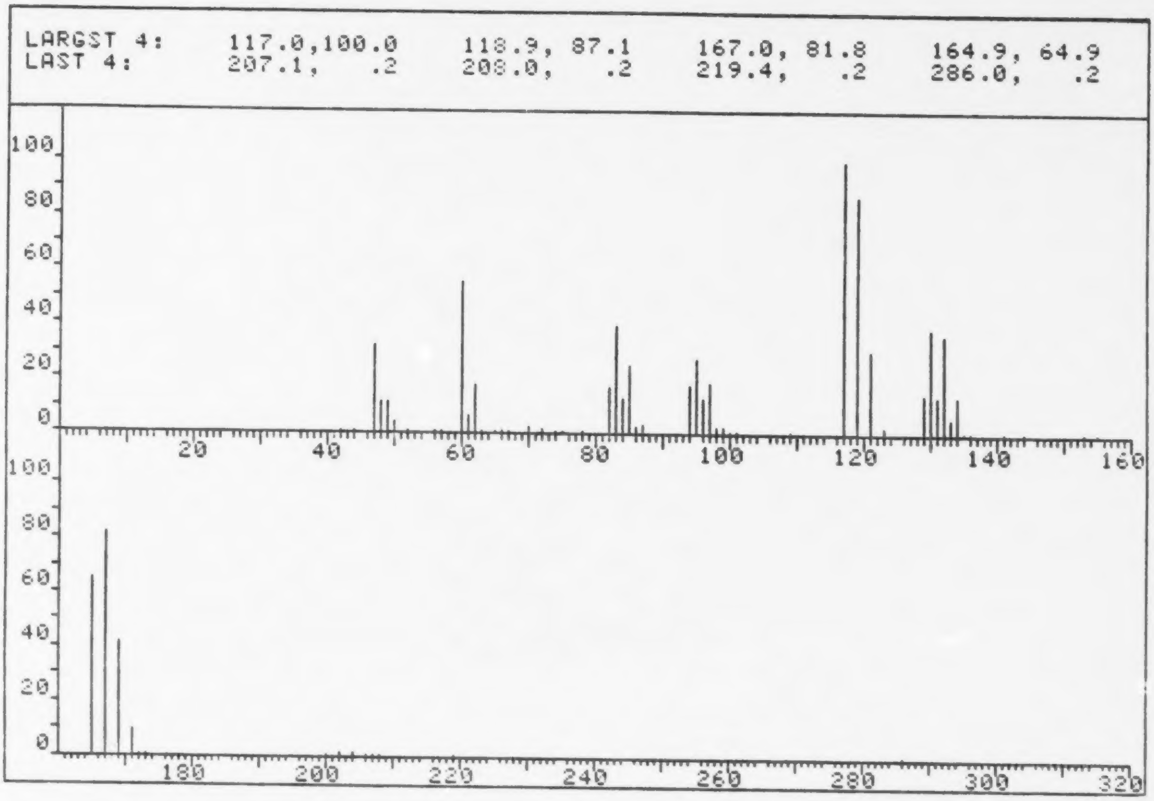


Figure B-3. Calibration curve for the determination of 1,3-dichloro-2-propanol by GC/MS.

Range: 9.0 - 86 ng
Correlation coefficient: 0.996
Slope: 6.7×10
y-Intercept: -1.5×10^{-1}



```
LARGST 4:    117.0,100.0    118.9, 87.1    167.0, 81.8    164.9, 64.9
LAST 4:      207.1,    .2   208.0,    .2   219.4,    .2   286.0,    .2
```

Figure B-4. Mass spectrum for pentachloroethane.

TABLE B-2. KEY IONS AND RELATIVE ABUNDANCES FOR PENTACHLOROETHANE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
42	.4	85	25.2	136	1.1
44	.2	86	2.6	141	.1
47	32.4	87	3.8	144	.2
48	11.7	94	18.2	153	.1
49	11.6	95	27.3	155	.1
50	4.2	96	13.0	165	64.9
52	.3	97	18.4	167	81.8
56	.3	98	2.5	169	41.4
57	.3	99	2.7	171	9.1
60	55.3	100	.2	172	.3
61	6.3	101	.1	173	.7
62	17.7	109	.2	200	.8
63	.2	117	100.0	202	1.4
65	1.1	119	87.1	204	1.0
66	1.5	121	30.5	206	.3
67	.6	123	2.6	207	.2
70	2.2	129	14.7	208	.2
72	1.4	130	39.0	219	.2
74	.4	131	14.0	286	.2
75	.2	132	36.5		
78	.2	133	5.5		
82	16.9	134	13.8		
83	39.2	135	.7		
84	12.8				

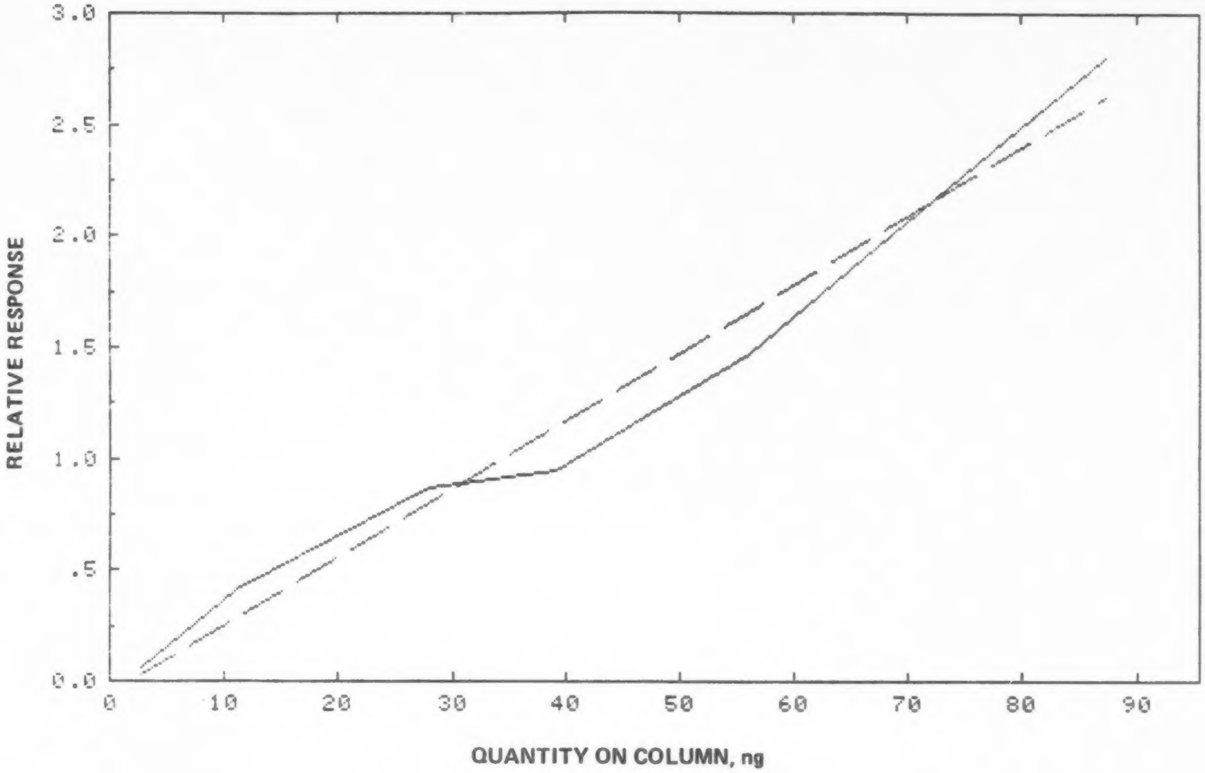


Figure B-5. Calibration curve for the determination of pentachloroethane by GC/MS.

Range: 28 - 87 ng
Correlation coefficient: 0.986
Slope: 3.1×10^{-2}
y-Intercept: -5.7×10^{-2}

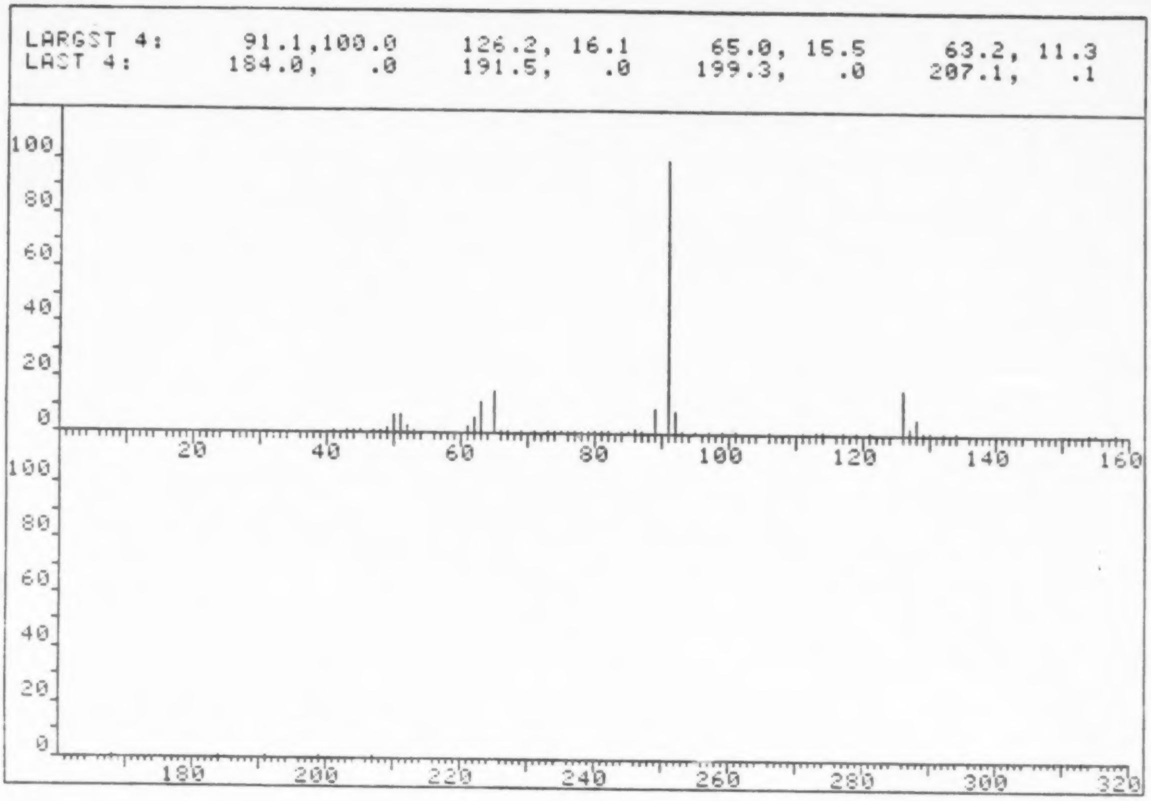


Figure B-6. Mass spectrum for benzyl chloride.

TABLE B-3. KEY IONS AND RELATIVE ABUNDANCES FOR BENZYL CHLORIDE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	.6	78	.1	126	16.1
43	.2	79	.0	127	2.0
44	.4	80	.1	128	5.6
45	.6	81	.1	129	.5
47	.3	82	.1	130	.0
48	.4	84	.4	132	.0
49	1.8	85	1.0	134	.0
50	6.6	86	1.3	154	.0
51	6.3	87	.7	155	.0
52	2.5	89	9.4	158	.0
53	.3	91	100.0	168	.0
61	2.4	92	7.8	184	.0
62	5.6	93	.3	191	.0
63	11.3	95	.1	199	.0
65	15.5	97	.2	207	.1
66	.9	99	1.1		
67	.1	101	.4		
69	.1	106	.0		
71	.1	111	.0		
73	1.2	113	.0		
74	1.2	114	.0		
75	1.2	117	.0		
76	.6	119	.1		
77	.4	121	.0		

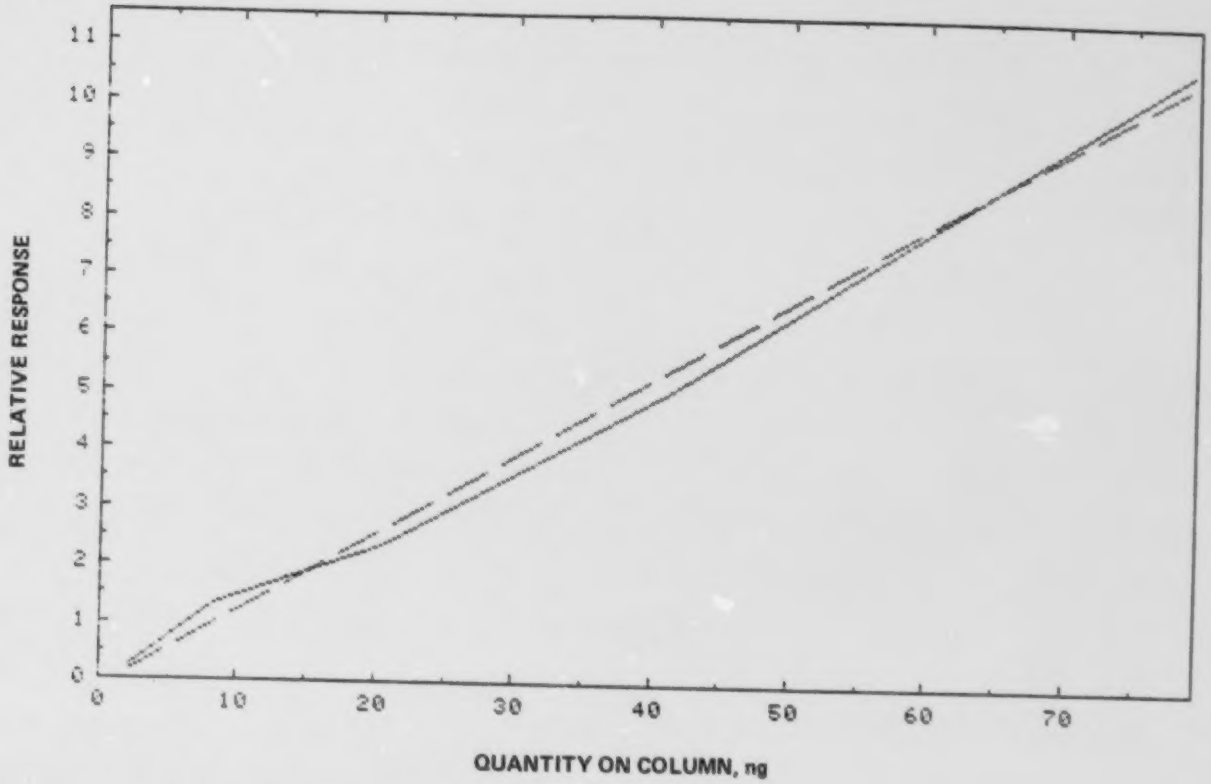
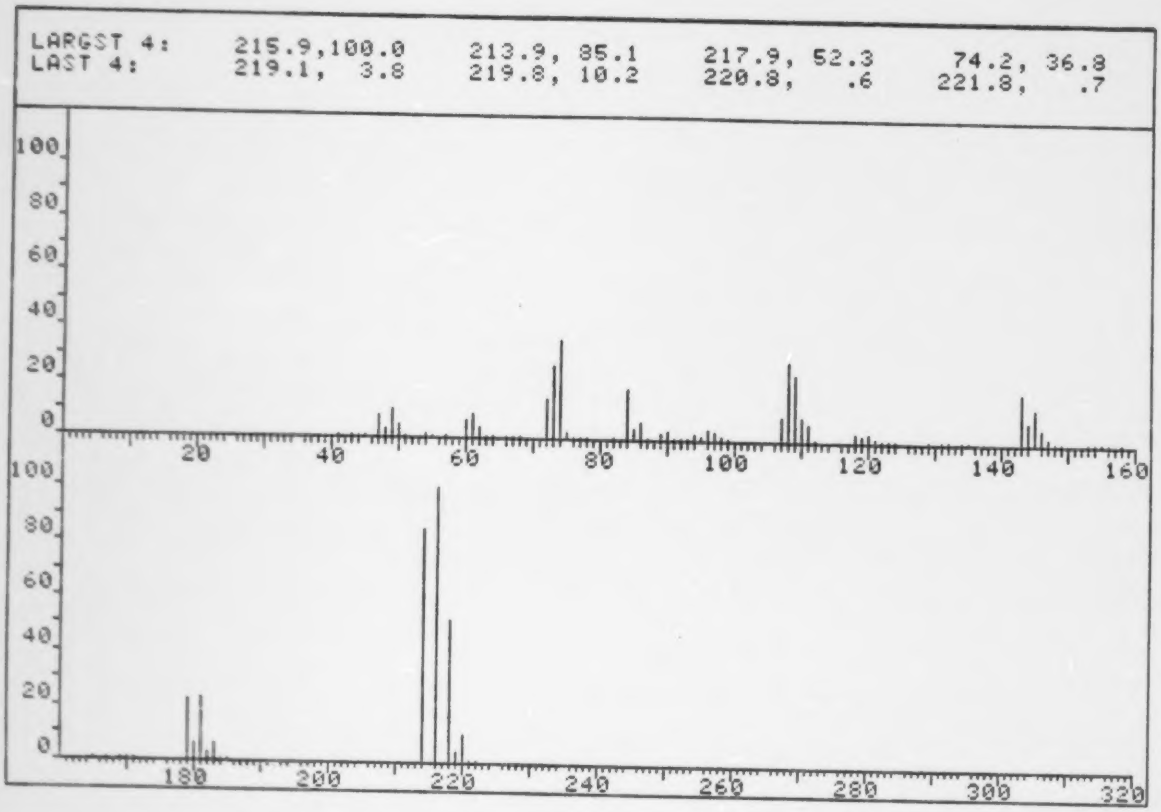


Figure B-7. Calibration curve for the determination of benzyl chloride by GC/MS.

Range: 8.2 - 79 ng
Correlation coefficient: 0.997
Slope: 1.3×10^{-1}
y-Intercept: -1.3×10^{-1}



```
LARGST 4:    215.9,100.0    213.9, 85.1    217.9, 52.3     74.2, 36.8
LAST 4:      219.1,   3.8   219.8, 10.2    220.8,    .6   221.8,    .7
```

Figure B-8. Mass spectrum for 1,2,4,5-tetrachlorobenzene.

TABLE B-4. KEY IONS AND RELATIVE ABUNDANCES FOR 1,2,4,5-TETRACHLOROBENZENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	.1	76	.1	112	.6	158	.2
43	.2	77	.2				
44	.2	78	.2	118	3.3	165	.3
45	.4	78	.0	119	2.5	167	.7
47	8.0	82	.9	120	3.0	169	.6
		84	18.5	121	1.6	170	.1
48	3.7	85	4.0	122	.9	171	.2
49	10.3	86	6.3	123	.3		
50	4.9	87	.5	124	.1	179	22.3
51	.3	89	2.7	129	.1	180	5.8
54	1.8			131	1.1	181	23.5
55	.8	90	3.0			182	2.5
57	.1	91	.7	132	.7	183	6.0
60	6.3	92	.2	134	.2	184	.6
61	9.2	93	.3	135	.0	185	.8
		94	2.7	143	18.9		
62	4.3	95	2.0	144	8.6	214	85.1
63	.5	96	4.6	145	13.5		
64	.2	97	3.6			216	100.0
66	.3	98	1.5	146	5.5	218	52.3
67	.2	99	.8	147	2.6	219	3.8
68	.3			148	.9	220	10.2
72	14.8	107	8.7	149	.2	221	.6
73	26.3	108	28.8	153	.2	222	.7
74	36.8	109	24.2	154	.7		
75	2.2	110	9.4	155	.2		
		111	6.8	156	.6		

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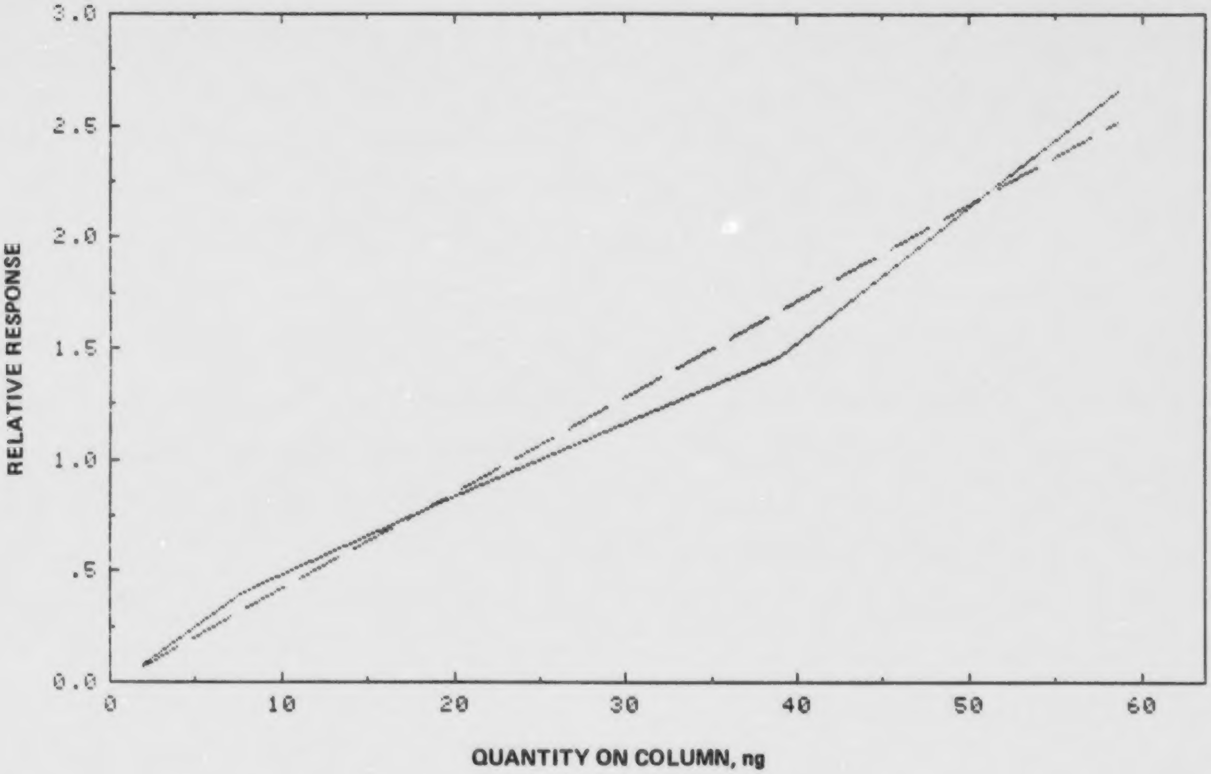

Figure B-9. Calibration curve for the determination of 1,2,4,5-tetrachlorobenzene by GC/MS.

Range: 2.0 - 59 ng
Correlation coefficient: 0.991
Slope: 4.3 x 10^{-2}
y-Intercept: -1.3 x 10^{-2}

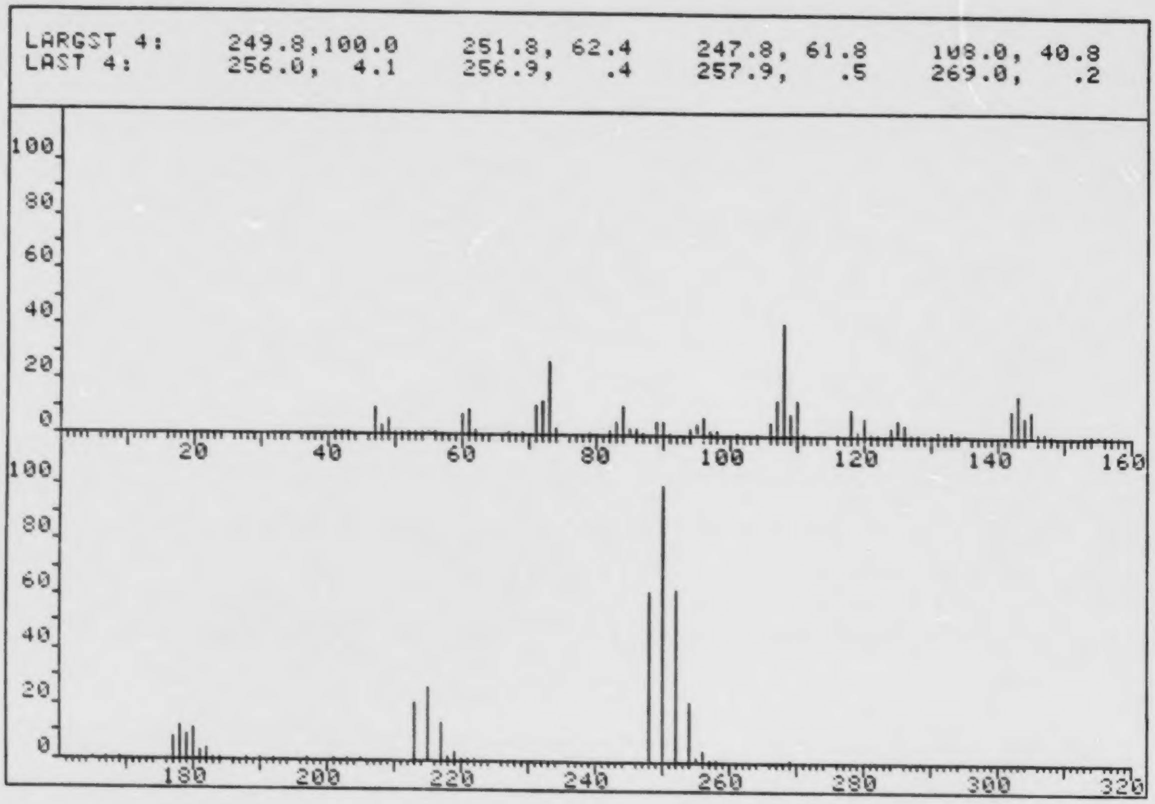

Figure B-10. Mass spectrum for pentachlorobenzene.

TABLE B-5. KEY IONS AND RELATIVE ABUNDANCES FOR PENTACHLOROBENZENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	.2	90	4.7	132	.8	188	.4
42	.6	91	1.3	133	1.5	190	.7
43	.3	94	2.8	134	.4	192	.4
47	10.1	95	4.4	135	.1	197	.1
		96	6.7	142	9.7	201	.4
48	3.3	97	1.4	143	15.5		
49	5.6	98	1.8	144	7.0	203	.6
50	.9	101	.2	145	9.9	205	.4
51	.0					213	20.7
52	.1					215	26.2
53	.7						
54	1.1	104	.5	146	1.8	217	13.3
55	.6	106	4.8	147	1.4	218	1.5
56	.4	107	13.5	148	.2	219	2.7
60	6.9	108	40.8	153	.9	220	.4
61	9.4	109	7.7	154	.8	221	.2
		110	13.2	155	.4	222	.2
62	1.6	111	1.1				
67	.4	116	.2			248	61.8
67	.1			156	.6	250	100.0
69	.1	118	9.6	157	.4	252	62.4
71	10.6			158	.2	254	21.4
72	11.8					255	1.7
73	27.0			165	.6	256	4.1
74	2.7	119	1.8	167	.6	257	.4
		120	6.2	169	.3		
79	.1	121	1.1			258	.5
		122	.8	177	8.0	269	.2
82	1.4	124	3.1	178	11.7		
83	5.0	125	5.9	179	8.6		
84	10.2	126	4.2	180	10.7		
85	2.7	127	.9	181	3.2		
86	2.6	128	.3	182	3.6		
87	.3	130	1.0	183	.5		
89	5.0	131	1.9	184	.4		

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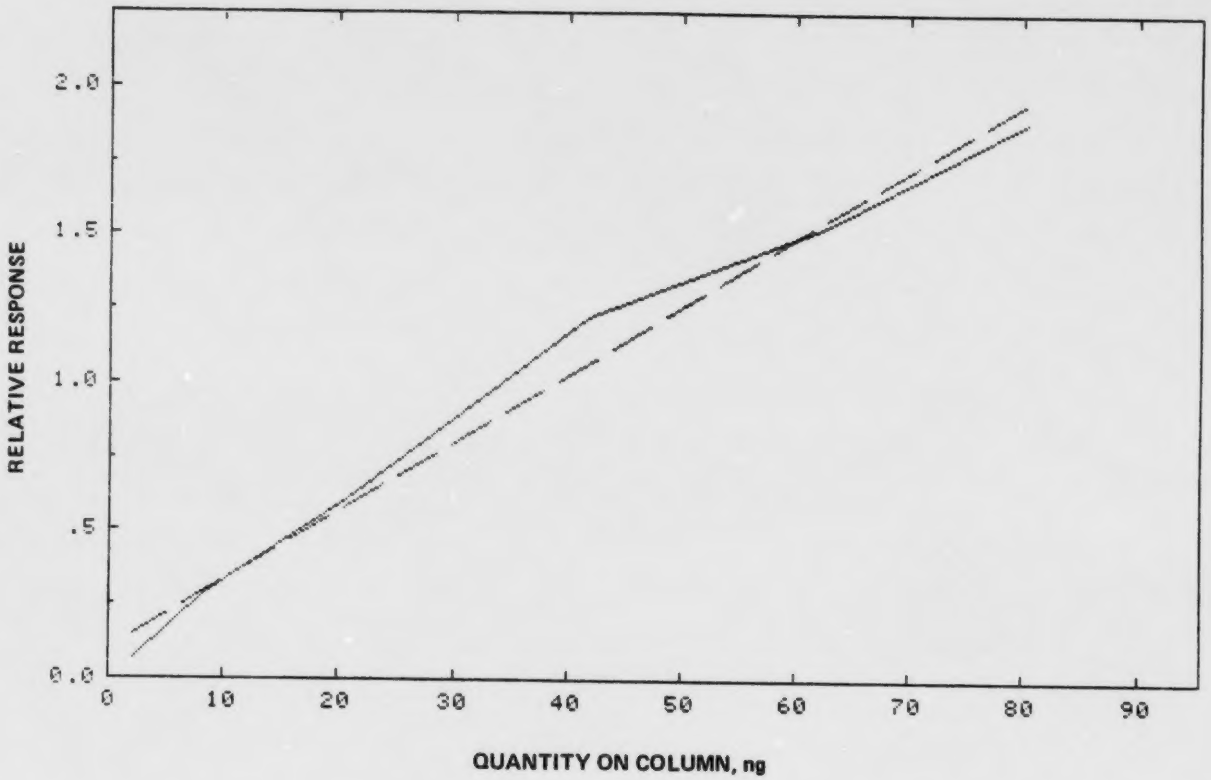

Figure B-11. Calibration curve for the determination of pentachlorobenzene by GC/MS.

Range: 8.3 - 80 ng
Correlation coefficient: 0.993
Slope: 2.3×10^{-2}
y-Intercept: 1.0×10^{-1}

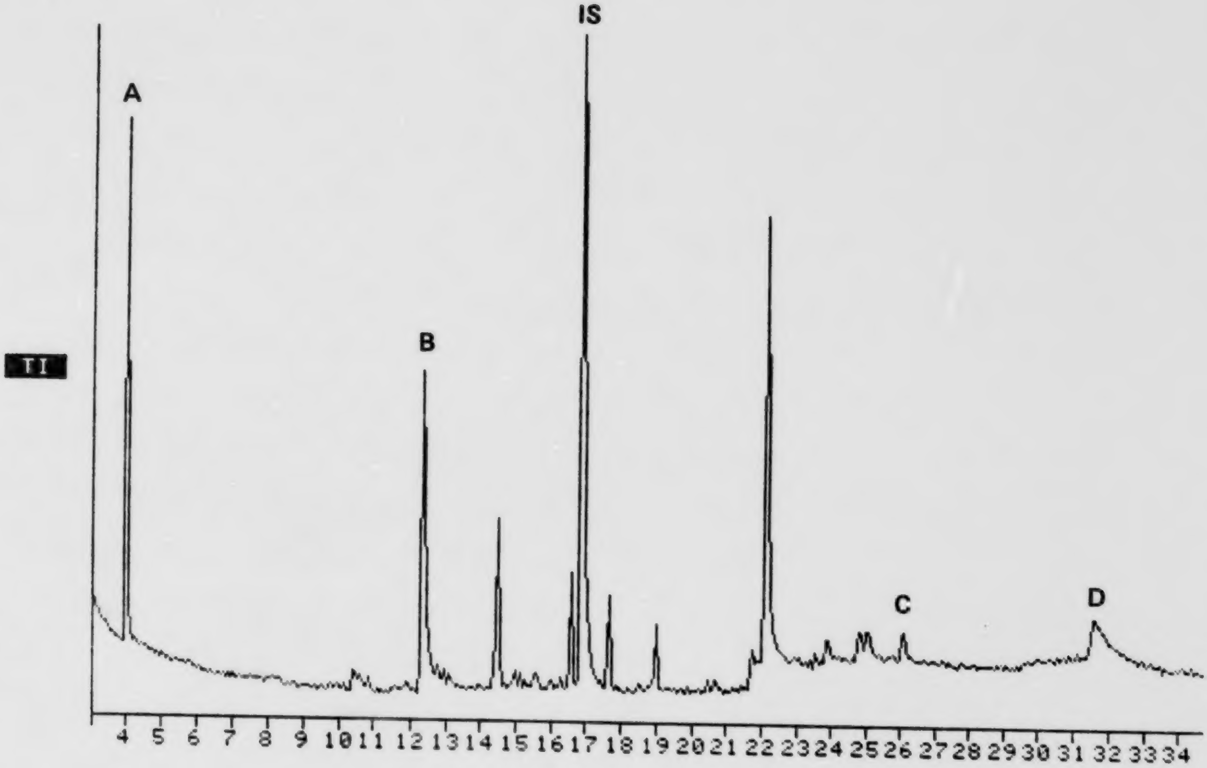

Figure B-12. Chromatogram by GC/MS for

(A) dimethyl sulfate(t_R = 4.0 min),
(B) 1,4-naphthoquinone(t_R = 12.3 min),
(C) 9,10-dimethyl-1,2-benzanthracene(t_R = 26.2 min), and
(D) dibenz[a,j]acridine(t_R = 31.6 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

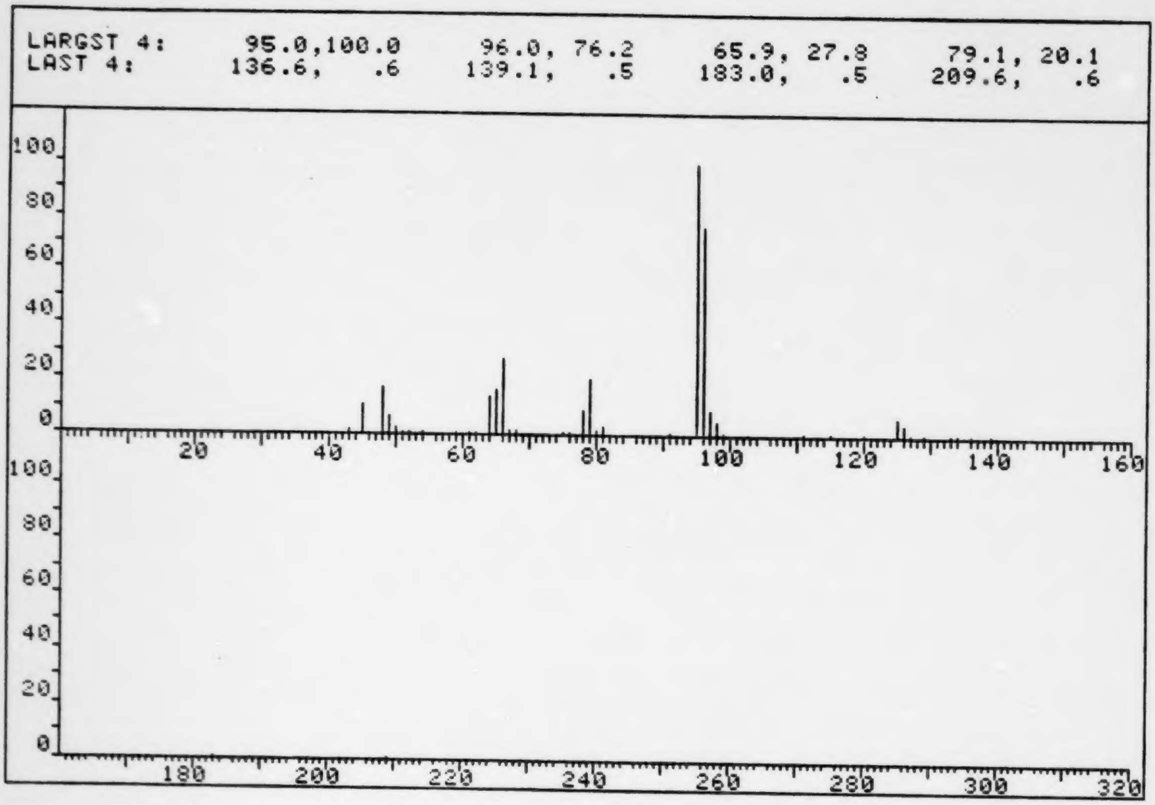

Figure B-13. Mass spectrum for dimethyl sulfate.

TABLE B-6. KEY IONS AND RELATIVE ABUNDANCES FOR DIMETHYL SULFATE

M/Z	Abundance	M/Z	Abundance
43	1.3	95	100.0
45	10.7	96	76.2
		97	9.3
48	17.2	98	4.7
49	6.1	99	.3
50	2.4		
51	.9	111	.6
52	1.0	115	.5
54	1.0		
59	.9	120	.5
61	1.0	125	6.1
		126	4.2
62	.7	127	1.0
64	13.6	129	.5
65	15.9		
66	27.8	133	.5
67	1.4	134	.4
68	2.0	136	.6
75	1.0	139	.5
76	1.0	183	.5
78	9.0		
79	20.1	209	.6
80	1.6		
81	3.0		
91	.5		

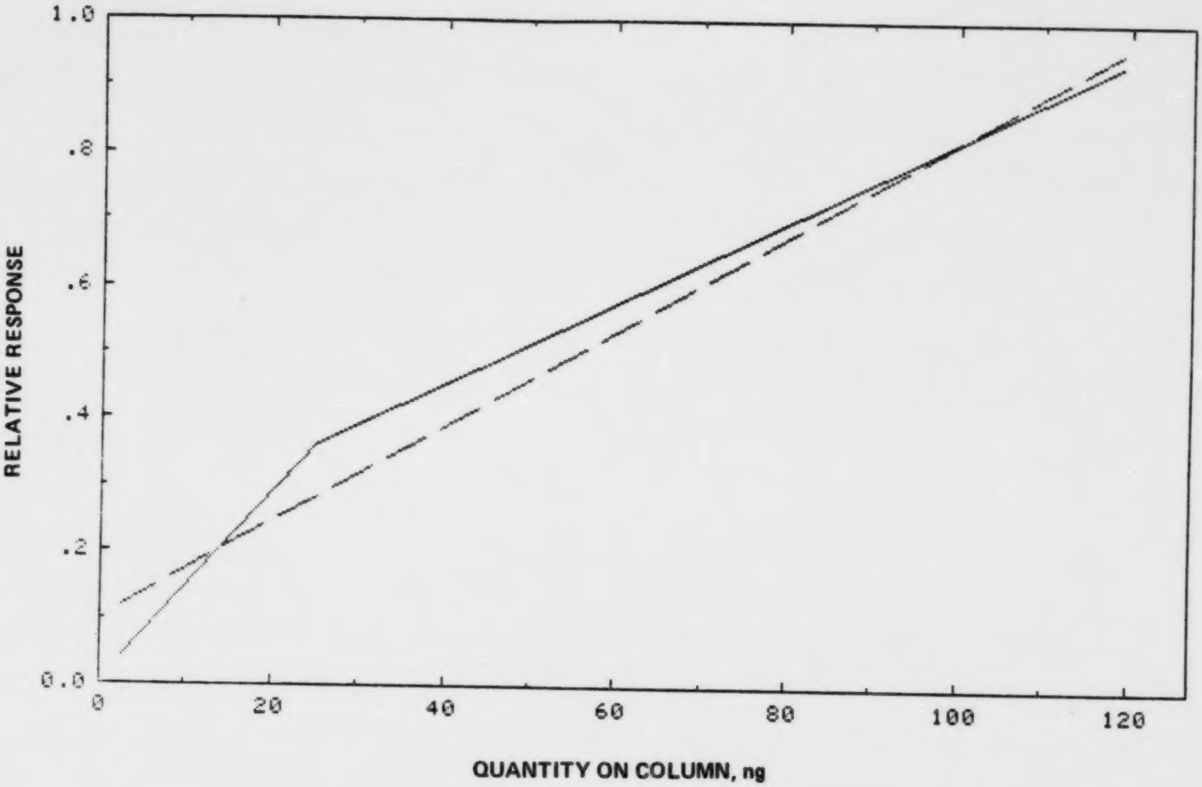

Figure B-14. Calibration curve for the determination of dimethyl sulfate by GC/MS.

Range: 16 - 120 ng
Correlation coefficient: 0.985
Slope: 7.2×10^{-3}
y-Intercept: 1.0×10^{-1}

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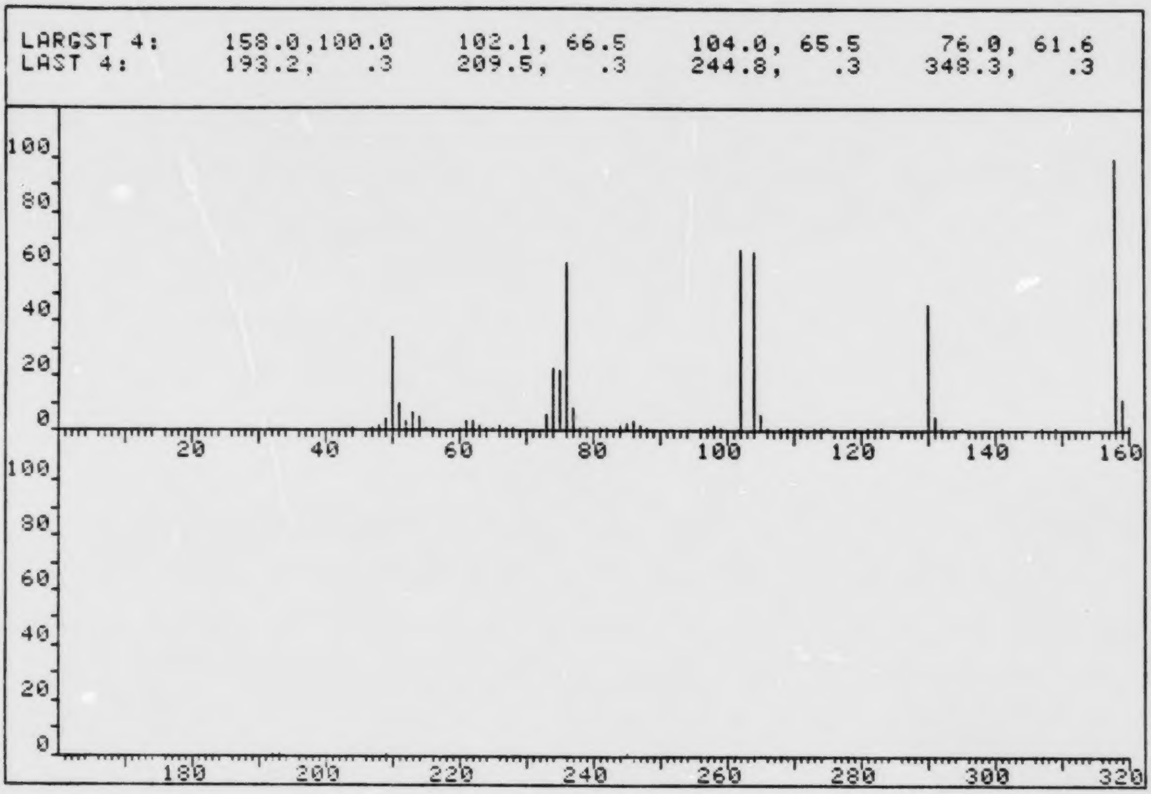


```
LARGST 4:     158.0,100.0     102.1, 66.5     104.0, 65.5      76.0, 61.6
LAST 4:       193.2,    .3    209.5,    .3    244.8,    .3    348.3,    .3
```

Figure B-15. Mass spectrum for 1,4-naphthoquinone.

TABLE B-7. KEY IONS AND RELATIVE ABUNDANCES FOR 1,4-NAPHTHOQUINONE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
44	.1	77	7.8	119	.1
47	.5	78	.8	121	.4
		79	.2	122	.8
48	1.3	81	.4	123	.4
49	4.1	82	.7	130	45.4
50	34.0	84	1.7	131	4.7
51	10.0	85	2.1		
52	3.9	86	3.2	132	1.1
53	6.5	87	1.9	135	.5
54	5.1	88	.4	141	.2
55	.3				
56	.5	96	.4	147	.4
60	.2	97	.5	149	.3
61	2.9	98	1.9	158	100.0
		99	.8	159	11.5
62	3.7	102	66.5		
63	2.0			160	1.5
64	.2	104	65.5		
65	.2	105	5.5	192	.4
66	1.8	106	.5	193	.3
67	.4	108	.8		
68	.4	109	1.0	209	.3
73	5.8	110	.4		
74	22.8	111	.4	245	.3
75	21.8	113	.4		
		114	.4	348	.3
76	61.6	115	.4		

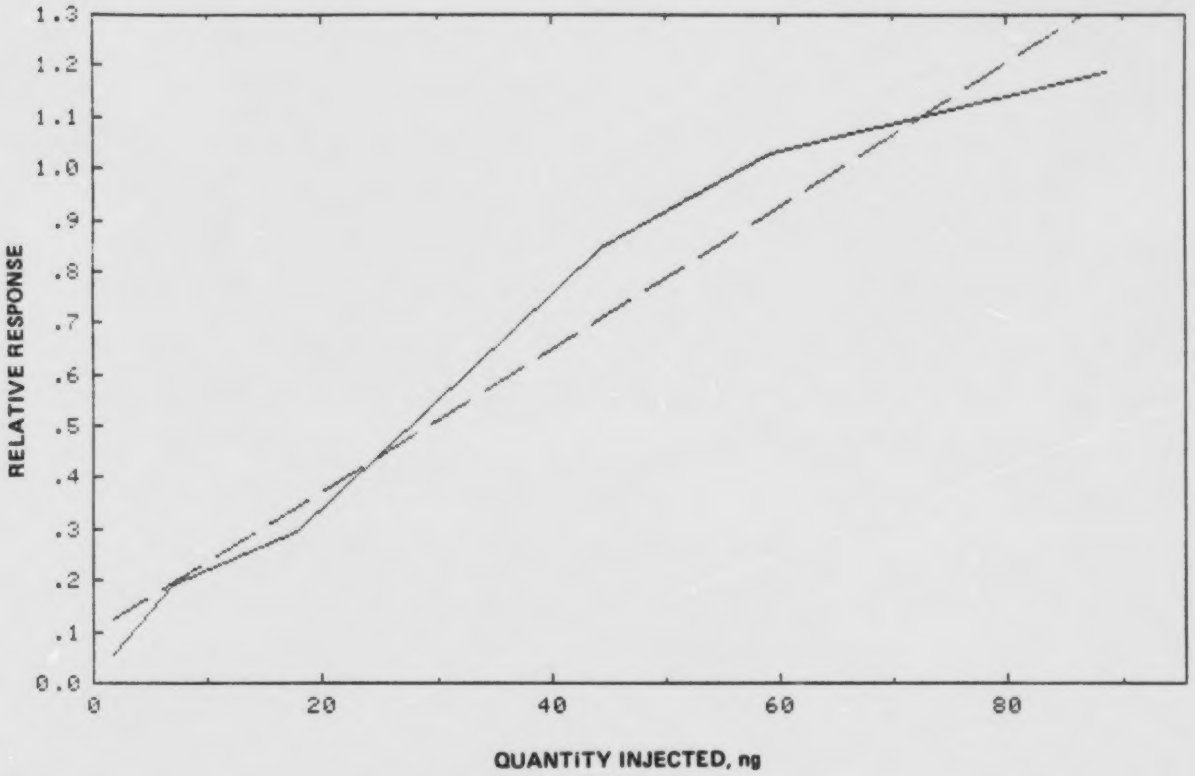
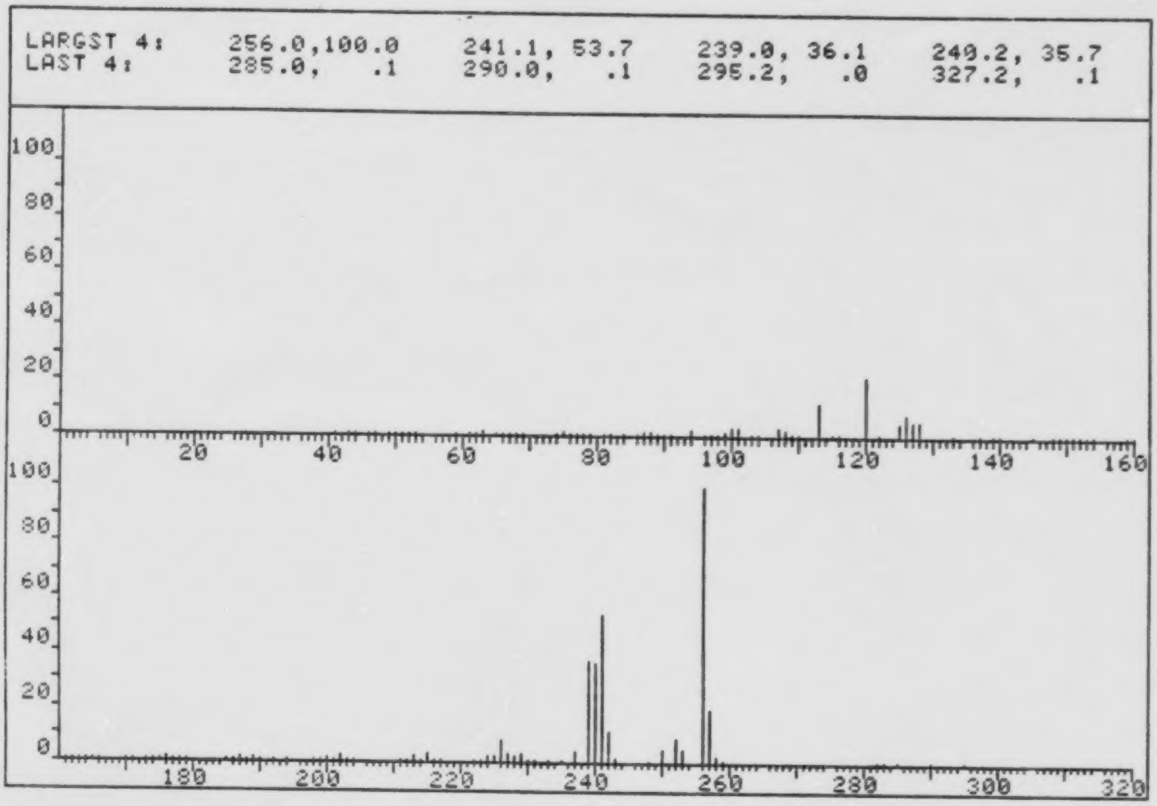


Figure B-16. Calibration curve for the determination of 1,4-naphthoquinone by GC/MS.

Range: 7.1 - 89 ng
Correlation coefficient: 0.975
Slope: 1.4×10^{-2}
y-Intercept: 9.8×10^{-2}



```
LARGST 4:     256.0,100.0     241.1, 53.7     239.0, 36.1     240.2, 35.7
LAST 4:       285.0,    .1    290.0,    .1    295.2,    .0    327.2,    .1
```

Figure B-17. Mass spectrum for 9,10-dimethyl-1,2-benzanthracene.

TABLE B-8. KEY IONS AND RELATIVE ABUNDANCES FOR 9,10-DIMETHYL-1,2-BENZANTHRACENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	.2	100	3.0	171	.1	230	.6
43	.7	101	3.6	173	.1	231	.2
44	.2	103	.4			233	.2
46	.3			174	.6	235	.5
47	.1	104	.5	175	.6		
		107	3.7	176	1.4	237	4.0
49	.5	108	2.3	177	.6	239	36.1
50	.9	109	.2	178	.8	240	35.7
51	1.2	110	.6	179	.2	241	53.7
52	.4			185	.4	242	10.8
53	.0	113	11.7	186	.5	243	1.1
59	.3	115	.8	187	1.6		
59	.4	116	.3			248	.8
61	.4					250	4.8
		120	21.3	188	.1	252	8.4
62	.9	122	.3	189	1.1	253	4.4
63	1.3	125	4.7	190	.2	256	100.0
65	.3	126	7.7	192	.2	257	19.1
66	.1	127	5.5	194	.1		
67	.4	128	5.4	198	.6	258	1.7
68	.5			199	.7	259	.2
69	.1	133	.1				
74	.8	137	.0			282	.2
75	1.4	139	.4	200	1.5	283	.1
		140	.0	201	.8	285	.1
76	1.1	145	.1				
77	1.3			202	1.7	290	.1
78	.4	148	.1	203	.3	295	.0
79	.1	149	.1	204	.1		
81	.5	150	1.0	211	.7	327	.1
82	.3	151	1.0	212	.6		
84	.1	152	.7	213	2.2		
86	.6	153	.3	214	.8		
87	1.6	154	.3	215	3.2		
88	1.9	159	.2				
89	.8			216	.7		
		160	.2	217	.2		
90	.2			222	.3		
91	.1	161	.2	223	.5		
94	1.5	162	.4	224	2.3		
94	2.3	163	.8	225	2.1		
96	.5	164	.5	226	7.6		
97	.2	165	.4	227	3.2		
98	.4	166	1	228	2.1		
99	1.7	170	.2	229	3.0		

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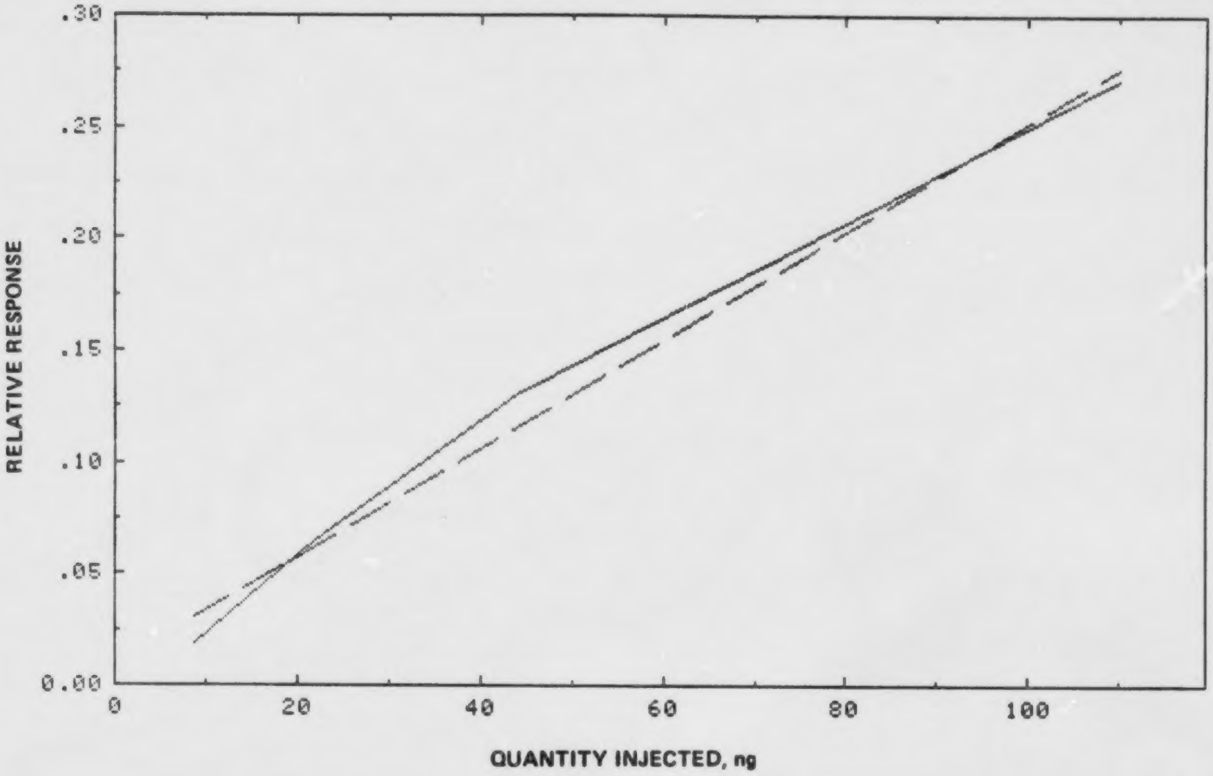
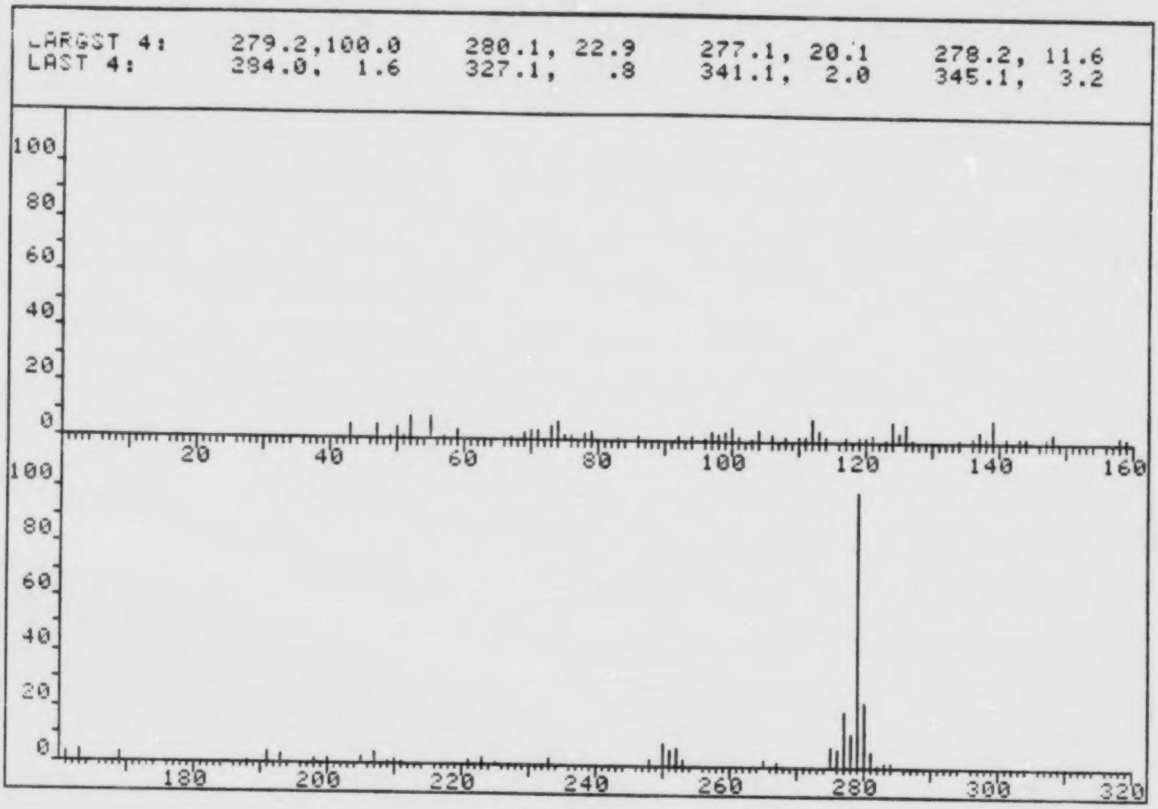


Figure B-18. Calibration curve for the determination of 9,10-dimethyl-1,2-benzanthracene by GC/MS.

Range: 22 - 110 ng
Correlation coefficient: 0.994
Slope: 2.4×10^{-3}
y-Intercept: 8.8×10^{-3}



```
LARGST 4:     279.2,100.0     280.1, 22.9     277.1, 20.1     278.2, 11.6
LAST 4:       284.0,  1.6     327.1,    .8    341.1,  2.0     345.1,  3.2
```

Figure B-19. Mass spectrum for dibenz[a,j]acridine.

TABLE B-9. KEY IONS AND RELATIVE ABUNDANCES FOR DIBENZ[a,j]ACRIDINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43	5.2	104	4.4	188	.8	281	5.6
47	4.8	106	2.4	191	4.0	282	.4
		108	1.6	193	3.2	283	1.2
49	.8	110	1.6	198	1.6	284	1.6
50	4.4	111	2.0	200	1.6		
51	.8	112	8.4			327	.8
52	8.0	113	4.0	205	2.0		
52	5.2	114	1.6	207	3.6	341	2.0
55	7.6	117	2.0	209	.4		
57	.4			210	1.6	345	3.2
59	3.2	119	1.6	211	.4		
		120	1.6				
67	.8	121	2.4	221	1.6		
69	2.4	123	.4	223	2.0		
70	3.2	124	7.2	225	.4		
71	2.8	125	3.6				
73	5.2	126	6.4	233	2.0		
74	6.4	127	.4				
75	1.6			248	2.0		
		134	.8	250	7.2		
76	2.0	136	1.6	251	5.2		
78	2.4	137	4.4	252	6.0		
79	3.2	138	1.6	253	2.0		
83	.4	139	7.6				
86	2.0	141	1.6	265	2.0		
		143	1.6	267	1.6		
92	2.0	144	2.0				
				275	6.8		
94	2.0	147	1.6	276	6.4		
96	.4	148	2.8	277	20.1		
97	3.6	158	2.4	278	11.6		
98	2.0	159	2.0	279	100.0		
98	2.4			280	22.9		
99	2.8	161	3.2				
100	5.2	163	4.0				
101	2.0	163	2.0				
103	.4	169	2.8				

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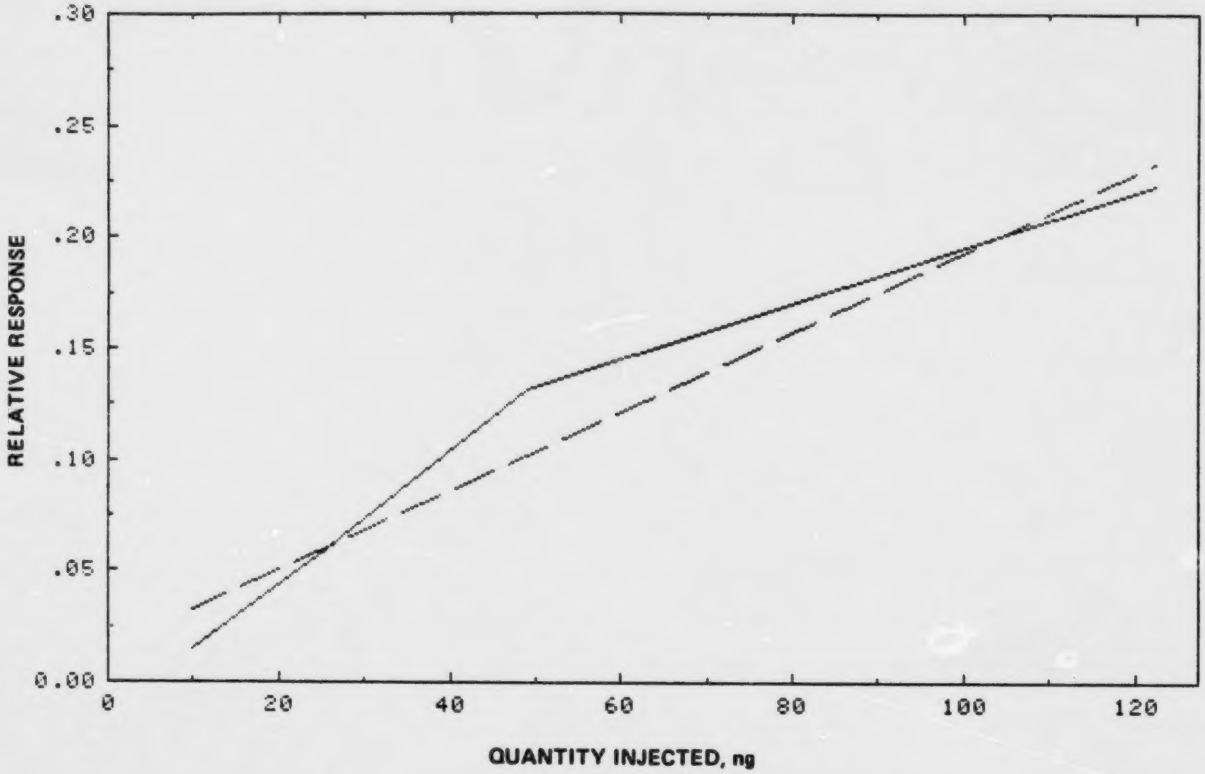


Figure B-20. Calibration curve for the determination of dibenz[a,j]acridine by GC/MS.

Range: 24 - 120 ng
Correlation coefficient: 0.974
Slope: 1.8×10^{-3}
y-Intercept: 1.5×10^{-2}

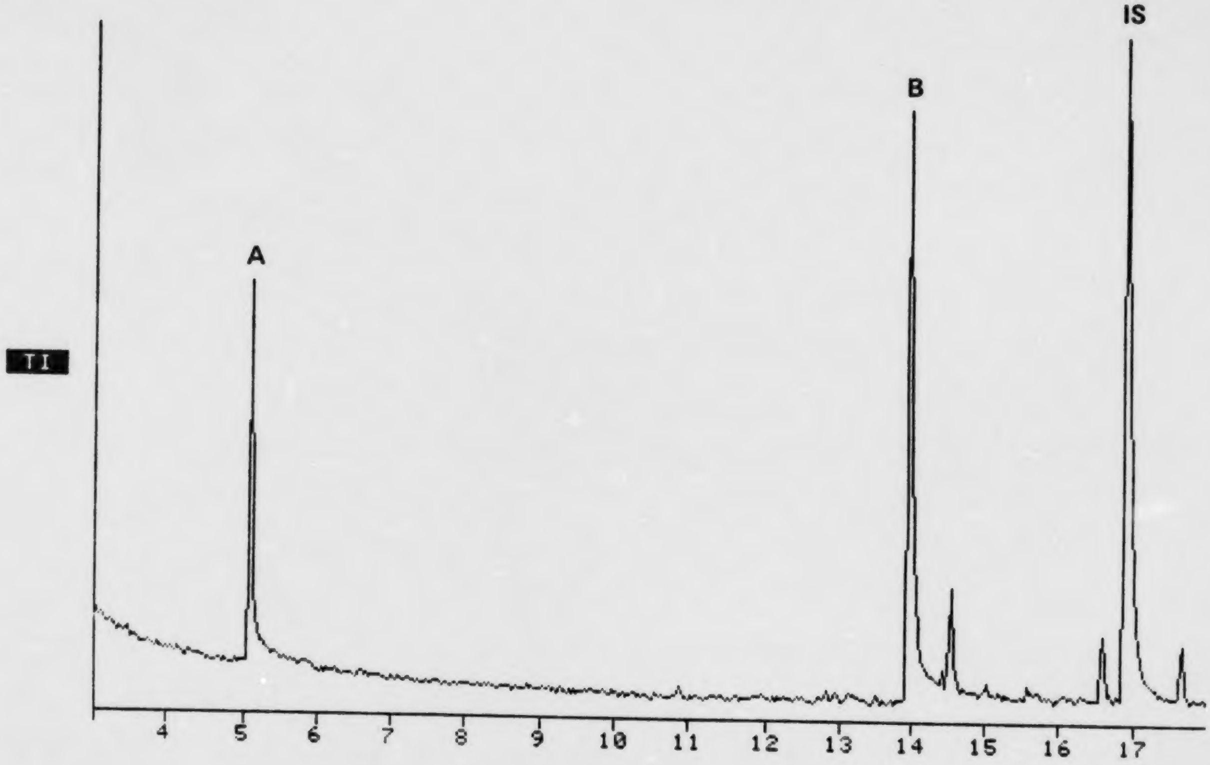
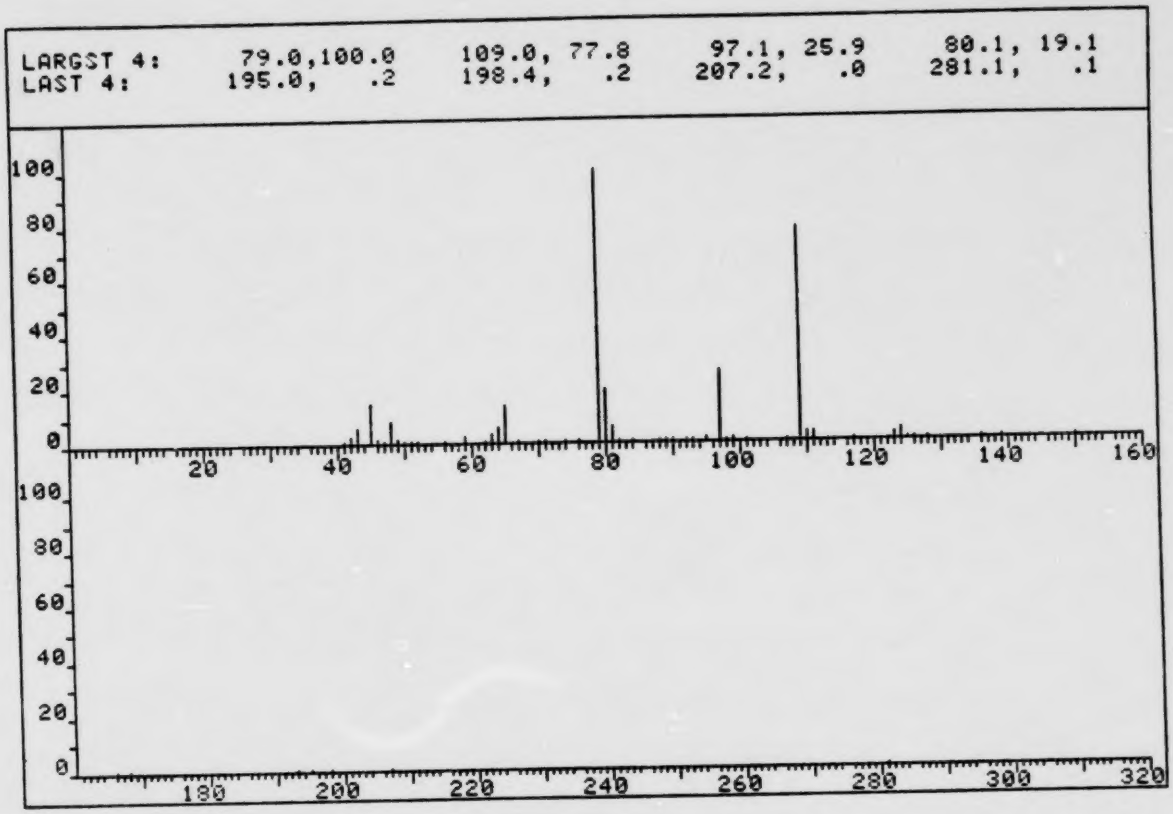


Figure B-21. Chromatogram by GC/MS for

(A) methanesulfonic acid ethyl ester(t_R = 5.2 min) and
(B) alpha-naphthylamine(t_R = 14.1 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C. 15 min isothermal



```
LARGST 4:     79.0,100.0     109.0, 77.8      97.1, 25.9      80.1, 19.1
LAST 4:      195.0,    .2    198.4,    .2    207.2,    .0    281.1,    .1
```

Figure B-22. Mass spectrum for methanesulfonic acid ethyl ester.

TABLE B-10. KEY IONS AND RELATIVE ABUNDANCES FOR METHANESULFONIC ACID ETHYL ESTER

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	.6	81	6.0	136	.2
42	2.6	82	.5	139	.2
43	5.7	84	.3		
45	14.9	88	.4	150	.1
46	1.3	89	.2		
47	1.0			166	.2
		90	.3	168	.2
48	8.6	92	.1		
49	1.5	93	.3	193	.1
50	.9	93	.3	195	.2
51	.8	95	1.6	198	.2
52	.5	97	25.9		
56	.4	98	.4	207	.0
59	2.2	99	1.3		
		101	.2	281	.1
62	.7				
63	3.6	107	.4		
64	6.0	109	77.8		
65	14.1	110	3.2		
67	.3	111	3.1		
70	.3	117	.0		
71	.3				
74	.3	123	2.3		
		124	4.1		
76	.3	125	.3		
79	100.0	126	.2		
80	19.1	128	.2		

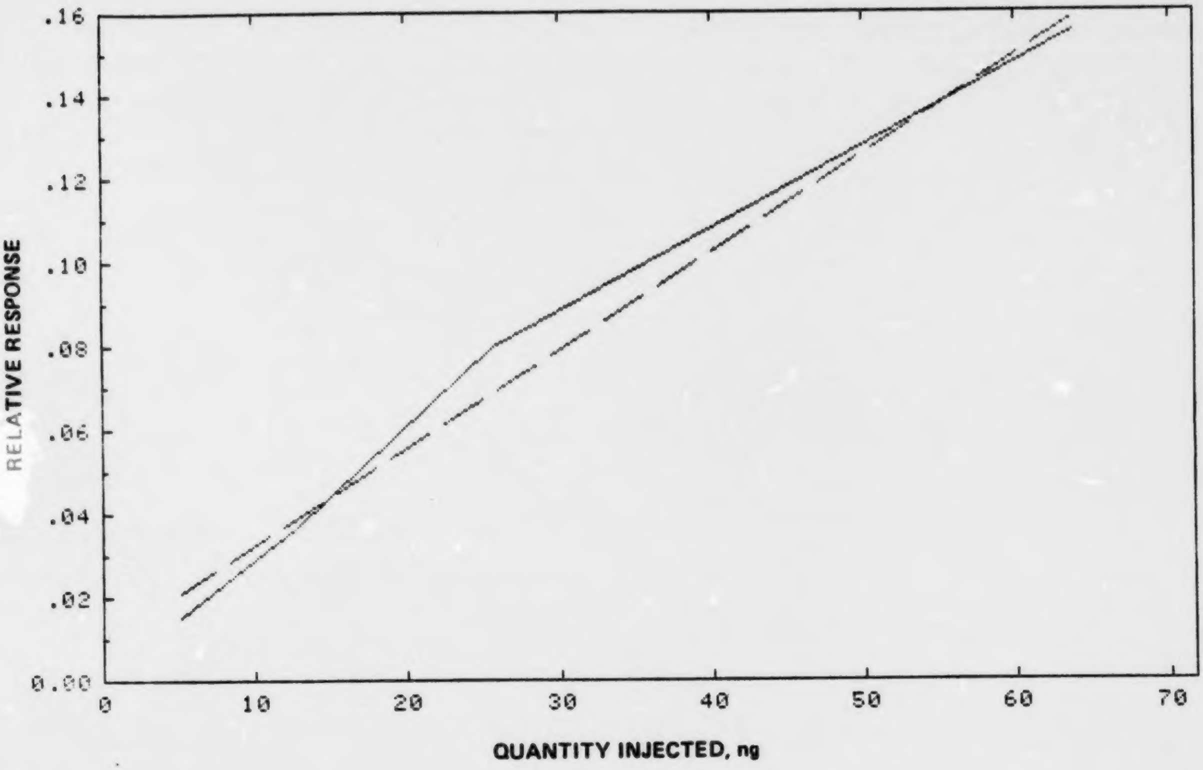
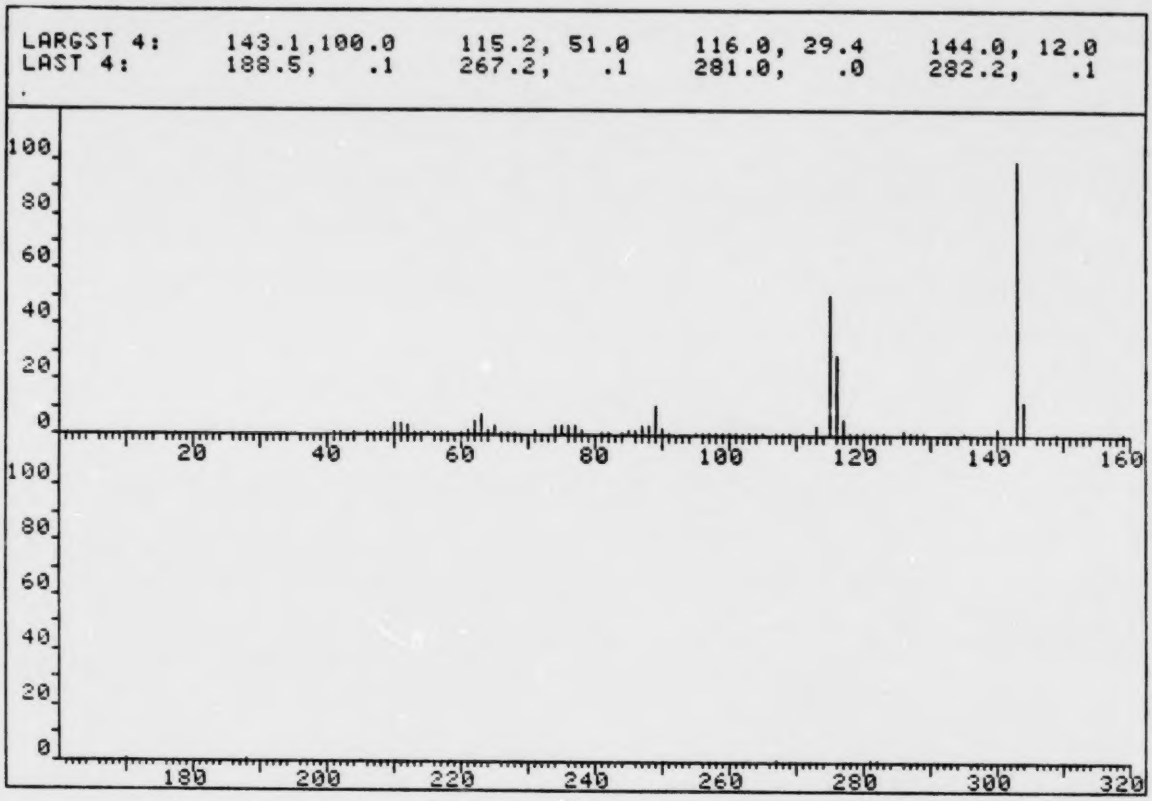


Figure B-23. Calibration curve for the determination of methanesulfonic acid ethyl ester by GC/MS.

Range: 13 - 64 ng
Correlation coefficient: 0.992
Slope: 2.4×10^{-3}
y-Intercept: 8.8×10^{-3}



```
LARGST 4:     143.1,100.0     115.2, 51.0     116.0, 29.4     144.0, 12.0
LAST 4:       188.5,    .1    267.2,    .1    281.0,    .0    282.2,    .1
```

Figure B-24. Mass spectrum for alpha-naphthylamine.

TABLE B-11. KEY IONS AND RELATIVE ABUNDANCES FOR *alpha*-NAPHTHYLAMINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	.3	71	1.8	103	1.0	144	12.0
42	.9	71	1.8				
44	.3	74	3.7	104	.8	149	.1
46	.3	75	2.9	105	.3	159	.1
47	.2			107	.1		
		76	2.9	108	.2	170	.1
48	.3	77	2.9	109	.1		
49	.3	78	1.3	111	.3	188	.1
50	4.1	81	.1	113	3.5		
51	4.5	82	.0	115	51.0	267	.1
52	3.1	84	.5	116	29.4		
53	.4	85	1.4	117	5.5	281	.0
54	.3	86	2.0			282	.1
55	.3	87	2.9	118	.5		
56	.3	88	3.1	119	.1		
57	.5	89	10.8	120	.1		
58	.9			121	.1		
60	.3	90	2.6	122	.2		
61	1.4	91	1.0	123	.1		
		95	.1	126	1.8		
62	4.9	96	.1	127	.7		
63	7.0	97	.3	128	.8		
64	1.9	98	.8	129	.1		
65	3.2	99	.6				
66	.5	100	.7	135	.1		
67	.1	101	1.1	140	2.7		
68	.3	102	.9	143	100.0		

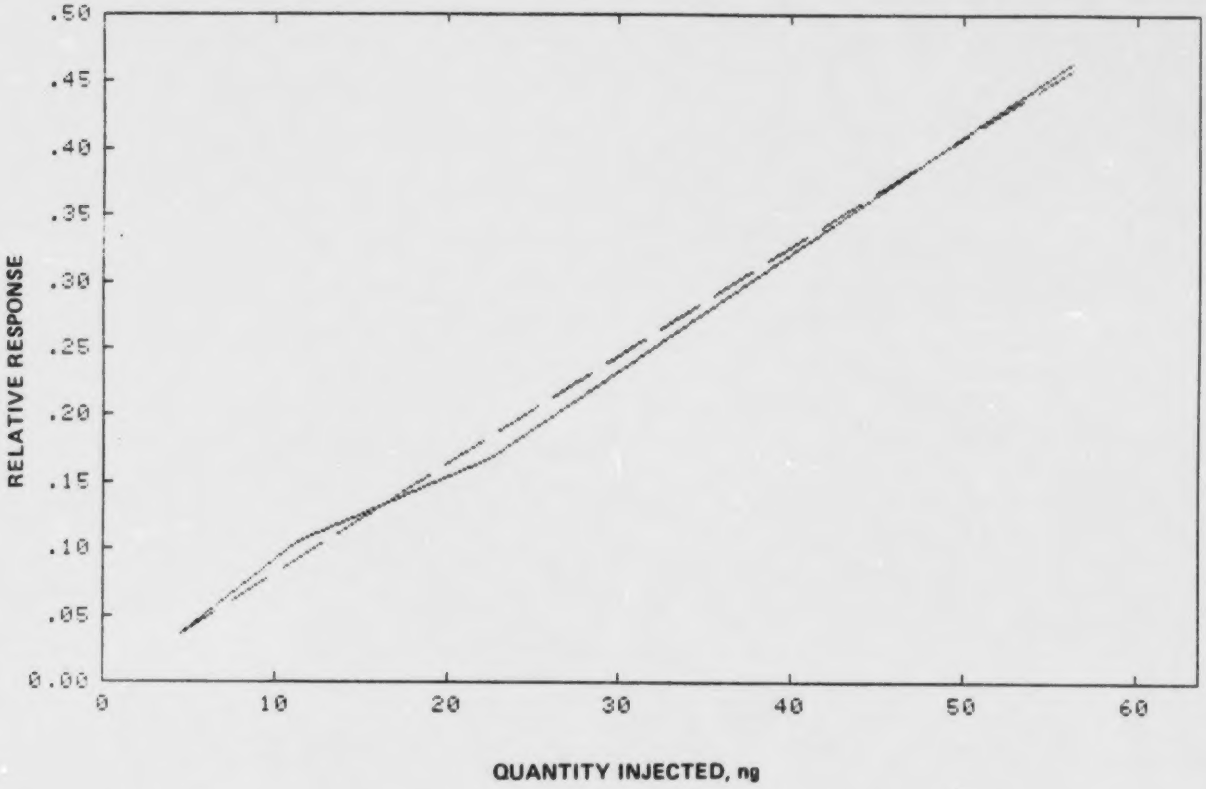


Figure B-25. Calibration curve for the determination of alpha-naphthylamine by GC/MS.

Range: 4.5 - 56 ng
Correlation coefficient: 0.998
Slope: 8.2×10^{-3}
y-Intercept: -9.0×10^{-5}

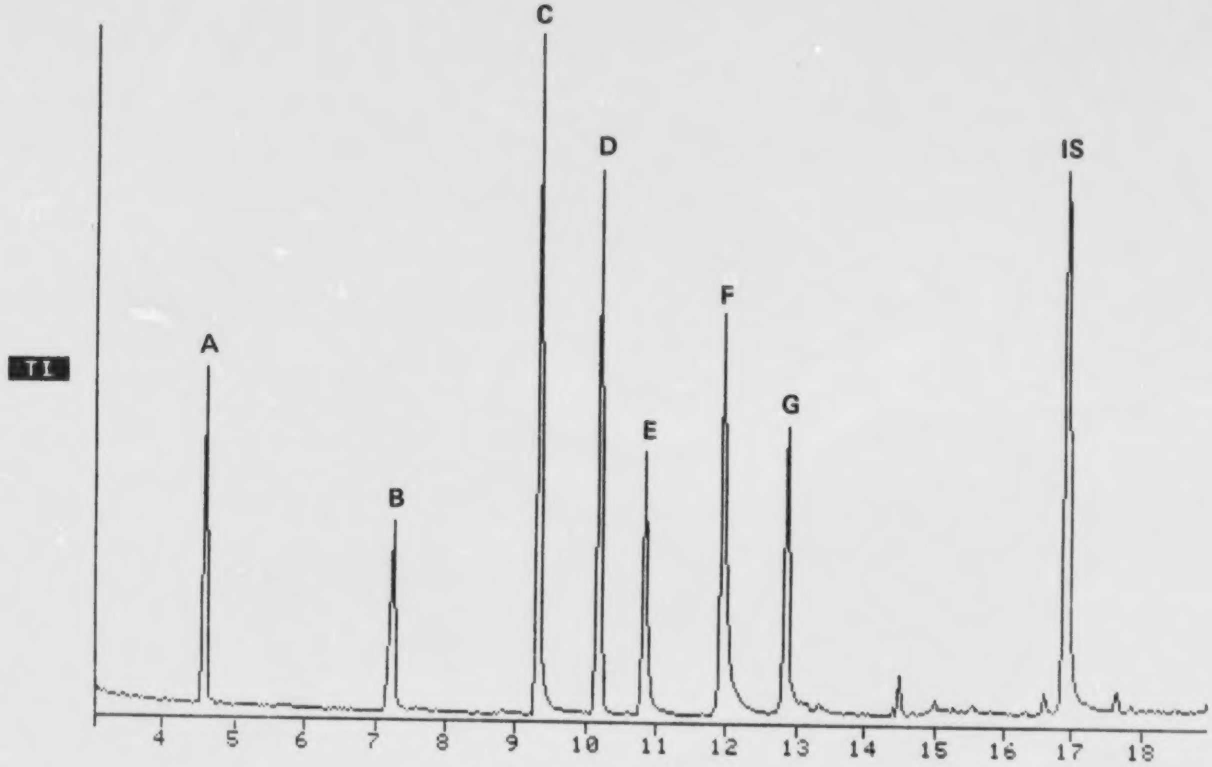
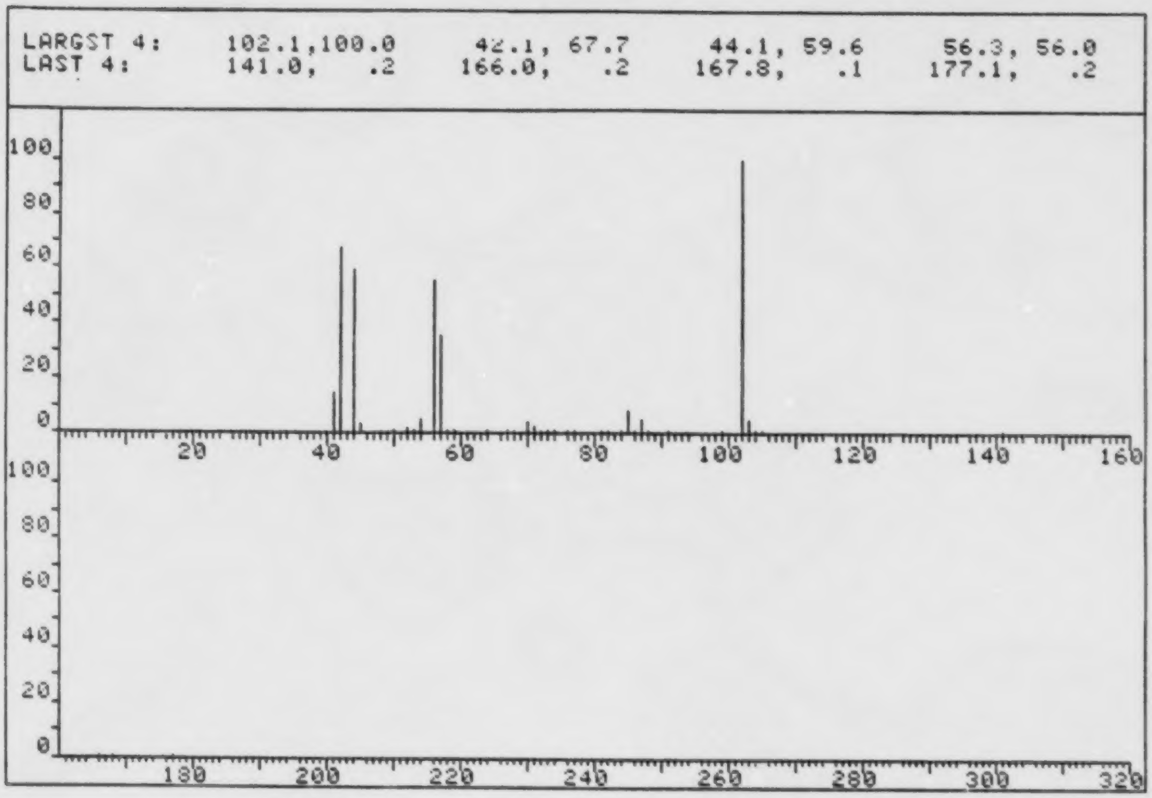


Figure B-26. Chromatogram by GC/MS for

(A) N-nitrosodiethylamine(t_R = 4.7 min),
(B) N-nitrosopyrrolidine(t_R = 7.2 min),
(C) 4-chloroaniline(t_R = 9.4 min),
(D) N-nitrosodibutylamine(t_R = 10.1 min).
(E) 3,4-diaminotoluene(t_R = 10.9 min),
(F) 2,4-diaminotoluene(t_R = 12.1 min), and
(G) m-dinitrobenzene(t_R = 12.9 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:     102.1,100.0      42.1, 67.7      44.1, 59.6      56.3, 56.0
LAST 4:       141.0,    .2    166.0,    .2    167.8,    .1    177.1,    .2
```

Figure B-27. Mass spectrum for N-nitrosodiethylamine.

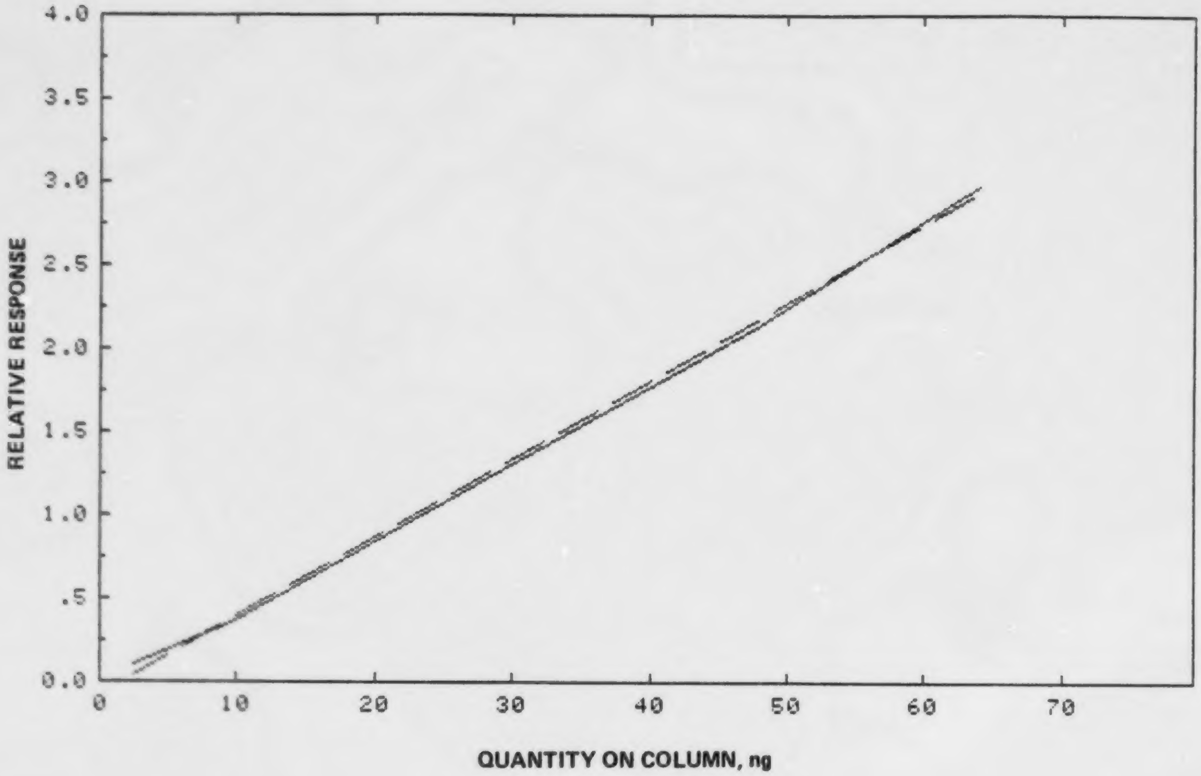


Figure B-28. Calibration curve for the determination of *N*-nitrosodiethylamine by GC/MS.

Range: 9.6 - 64 ng
Correlation coefficient: 0.999
Slope: 4.7×10^{-2}
y-Intercept: -6.8×10^{-2}

TABLE B-12. KEY IONS AND RELATIVE ABUNDANCES OF N-NITROSODIETHYLAMINE

M/Z	Abundance	M/Z	Abundance
41	14.3	84	1.2
42	67.7	85	7.8
44	59.6	86	.5
45	3.4	87	5.2
50	.1	88	.1
52	1.6	91	.2
53	.9	99	.2
54	5.1	102	100.0
56	56.0	103	5.0
57	35.6	104	.4
58	1.1	105	.2
59	.9	141	.2
64	.3	166	.2
67	.4	168	.1
68	.2	177	.2
70	4.0		
71	2.5		
72	.6		
73	.7		
74	.5		
76	.2		
77	.2		
81	.3		
82	.1		

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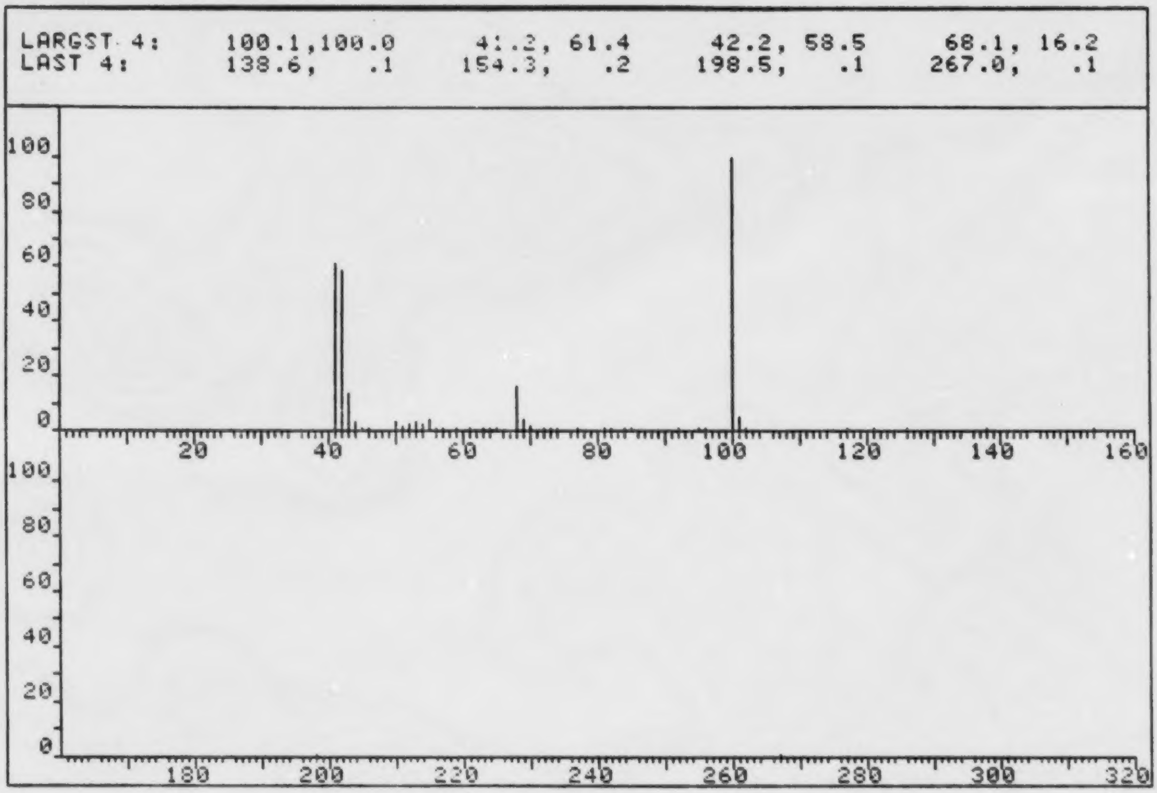


```
LARGST 4:     100.1,100.0      41.2, 61.4      42.2, 58.5      68.1, 16.2
LAST 4:       138.6,    .1    154.3,    .2    198.5,    .1    267.0,    .1
```

Figure B-29. Mass spectrum for N-nitrosopyrrolidine.

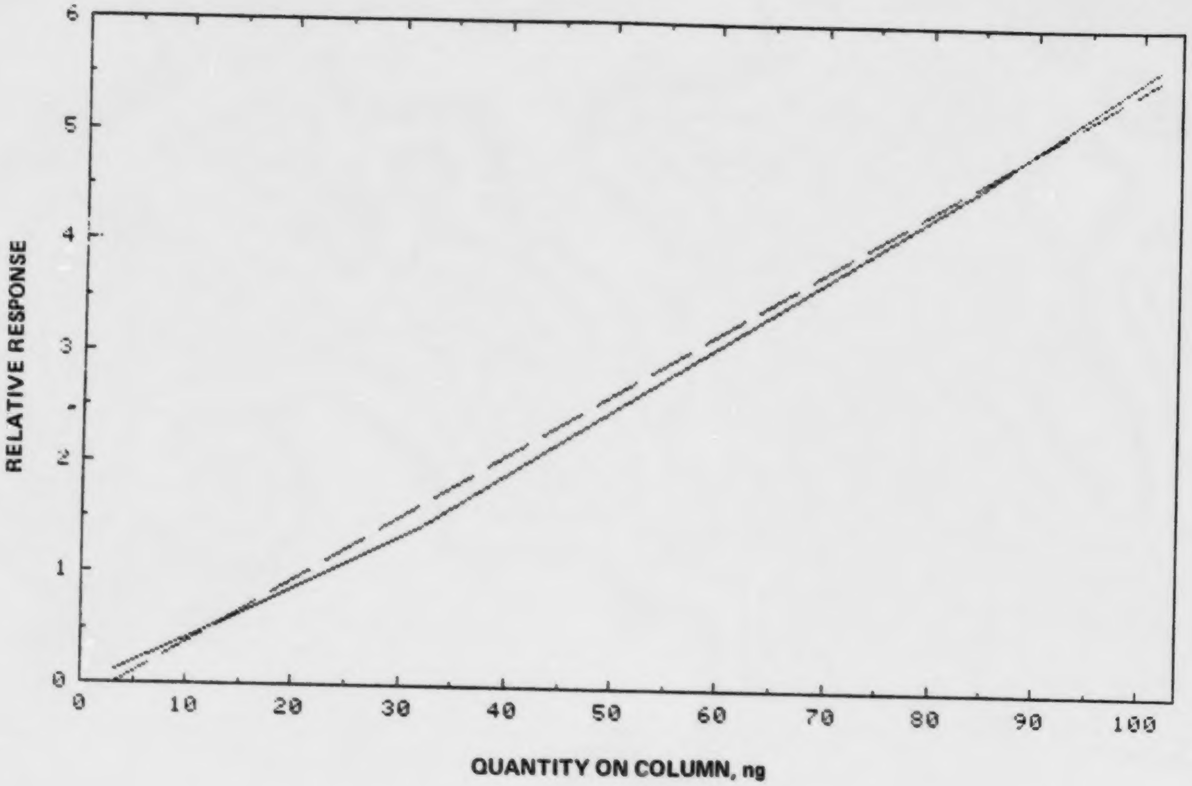
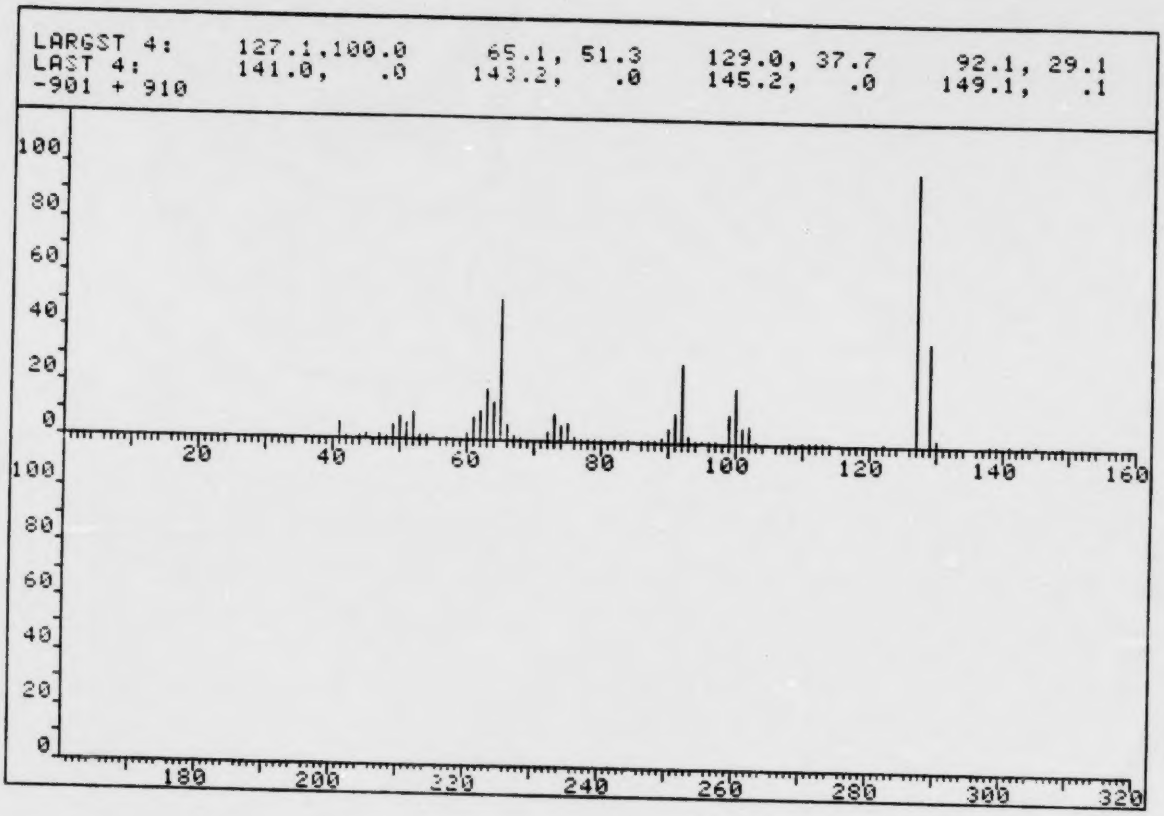


Figure B-30. Calibration curve for the determination of N-nitrosopyrrolidine by GC/MS.

Range: 13 - 100 ng
Correlation coefficient: 0.998
Slope: 5.7×10^{-2}
y-Intercept: -1.9×10^{-1}

TABLE B-13. KEY IONS AND RELATIVE ABUNDANCES OF N-NITROSOPYRROLIDINE

M/Z	Abundance	M/Z	Abundance
41	61.4	77	.1
42	58.5	81	.2
43	13.9	82	.1
44	2.9	84	.3
45	.7	85	.2
46	.3		
		92	.2
50	2.8	95	.2
51	1.9	96	.1
52	2.3	100	100.0
53	3.8	101	4.9
54	2.7	102	.4
55	4.3		
56	.9	117	.1
57	.4		
59	.2	121	.1
61	.2	126	.1
63	.6	138	.1
64	.6		
65	.4	154	.2
68	16.2		
69	4.5	198	.1
70	1.5		
72	.2	267	.1
73	.3		
74	.2		



```
LARGST 4:     127.1,100.0      65.1, 51.3     129.0, 37.7      92.1, 29.1
LAST 4:       141.0,    .0    143.2,    .0    145.2,    .0    149.1,    .1
-901 + 910
```

Figure B-31. **Mass spectrum for 4-chloroaniline.**

TABLE B-14. KEY IONS AND RELATIVE ABUNDANCES FOR 4-CHLOROANILINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	5.4	74	5.5	103	.7
42	1.2	75	6.9		
44	1.0			108	.2
45	1.9	76	1.3	110	.6
47	1.5	77	.3	111	.4
		78	.6	112	.3
48	1.0	79	.1	113	.1
49	5.0	80	.2	114	.1
50	8.3	82	.1		
51	5.8	84	.9	122	.0
52	10.1	86	1.2	127	100.0
53	1.6	87	.8	129	37.7
54	1.7	88	1.3	130	2.1
55	.1	89	1.4		
57	.1			138	.0
60	2.3	90	5.0	139	.0
61	8.2	91	10.7	141	.0
		92	29.1	143	.0
62	10.9	93	2.1	145	.0
63	18.5	94	.1		
64	14.1	95	.1	149	.1
65	51.3	96	.2		
66	6.1	97	.4		
67	1.4	99	10.8		
68	.1	100	20.5		
72	2.8	101	5.4		
73	9.8	102	6.4		

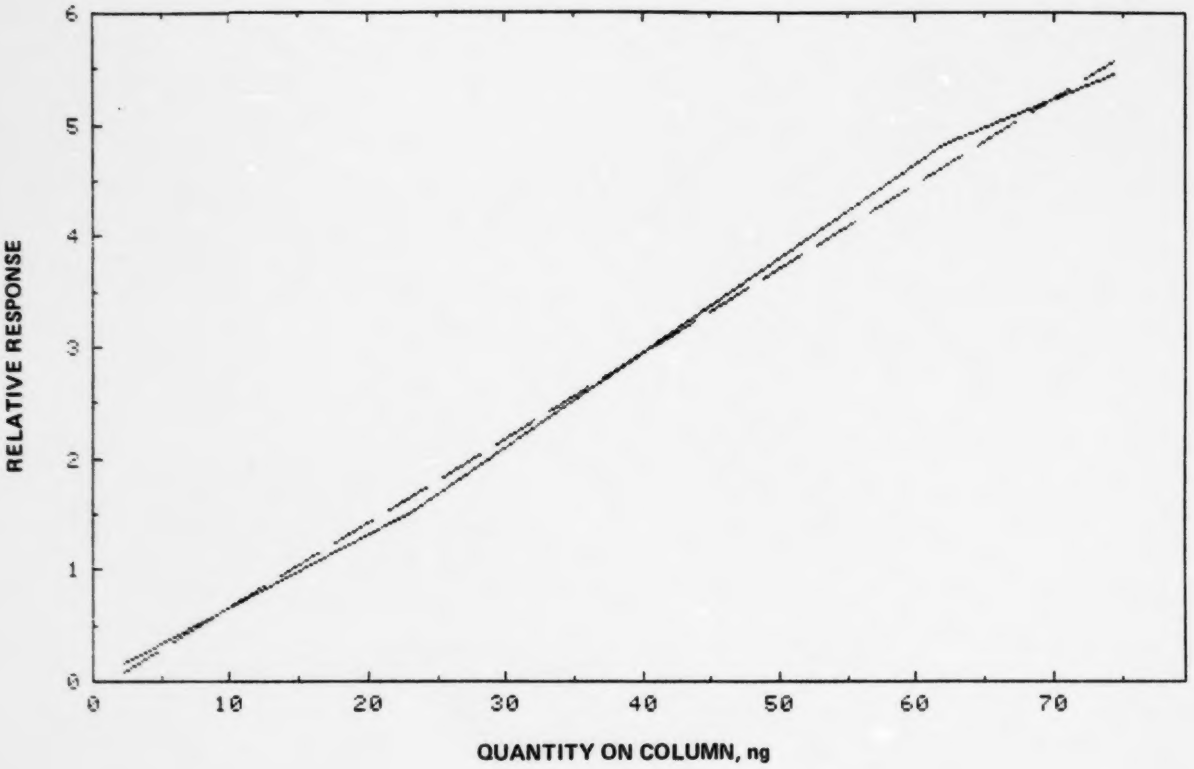
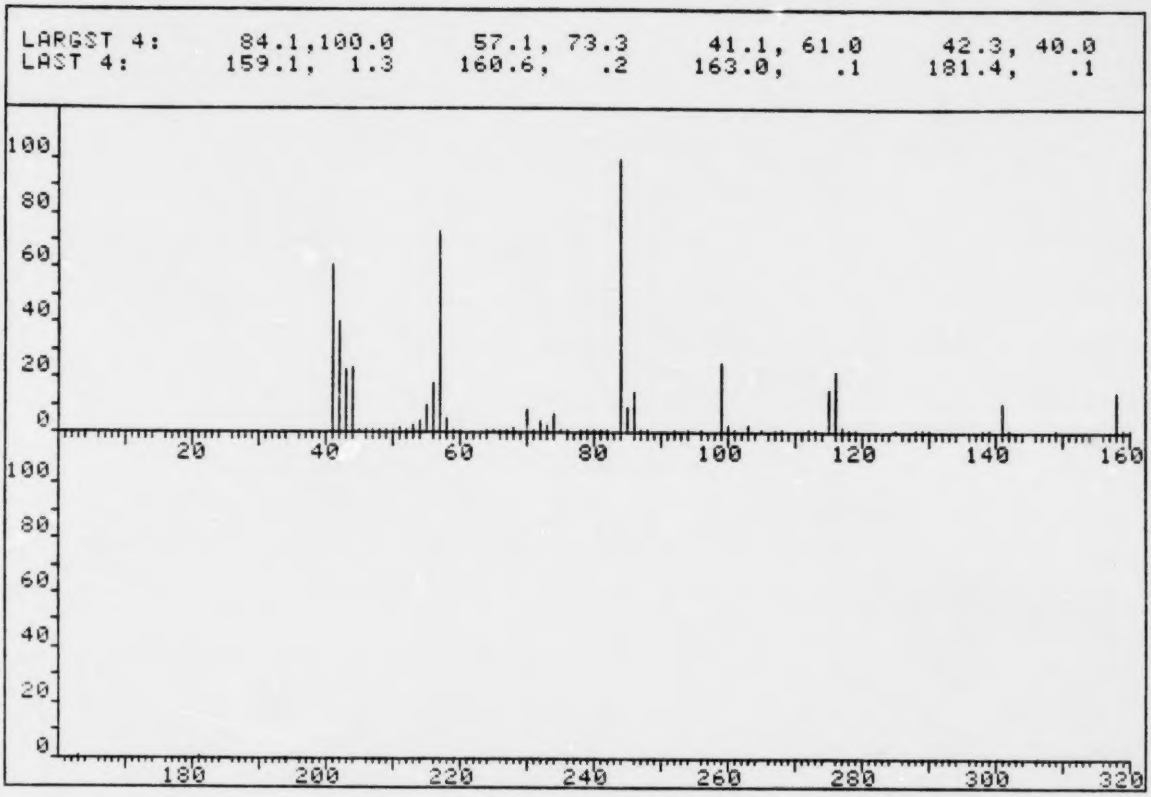


Figure B-32. Calibration curve for the determination of 4-chloroaniline by GC/MS.

Range: 9.3 - 74 ng
Correlation coefficient: 0.998
Slope: 7.6 x 10^{-2}
y-Intercept: -9.5 x 10^{-2}



```
LARGST 4:     84.1,100.0     57.1, 73.3     41.1, 61.0     42.3, 40.0
LAST 4:      159.1,  1.3    160.6,   .2    163.0,   .1    181.4,   .1
```

Figure B-33. Mass spectrum for N-nitrosodibutylamine.

TABLE B-15. KEY IONS AND RELATIVE ABUNDANCES FOR N-NITROSODIBUTYLAMINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	61.0	70	8.4	105	.1	181	.1
42	40.0	71	.8	107	.1		
43	22.5	72	4.5	108	.2		
44	23.9	73	2.7	112	1.1		
45	1.2	74	6.7	113	.2		
46	.3	75	.3	115	15.1		
47	.7			116	21.8		
		76	.1	117	1.5		
48	.3	78	.1				
49	.1	79	.2	118	.2		
50	.8	80	.3	119	.1		
51	1.4	81	.3	125	.1		
52	1.1	82	.7	128	.1		
53	2.6	84	100.0	129	.7		
54	4.3	85	8.9	130	.1		
55	9.9	86	14.4				
56	17.8	87	.9	138	.1		
57	73.3	88	.3	139	.1		
58	5.0			141	10.3		
59	.7	92	.1	142	1.0		
60	.5	94	.1				
		96	.3	149	.1		
64	.3	99	25.3	158	14.3		
65	.2	100	2.1	159	1.3		
66	.1	101	1.1				
67	.8	103	2.8	160	.2		
68	1.6			163	.1		

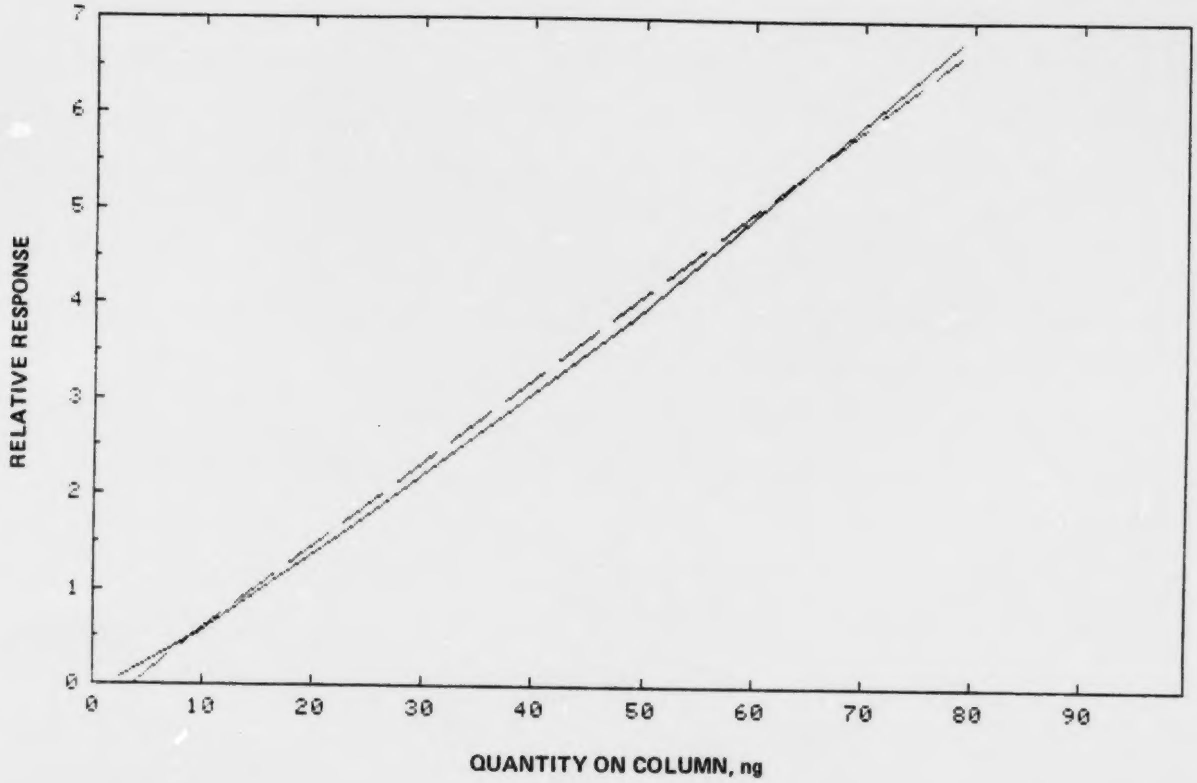
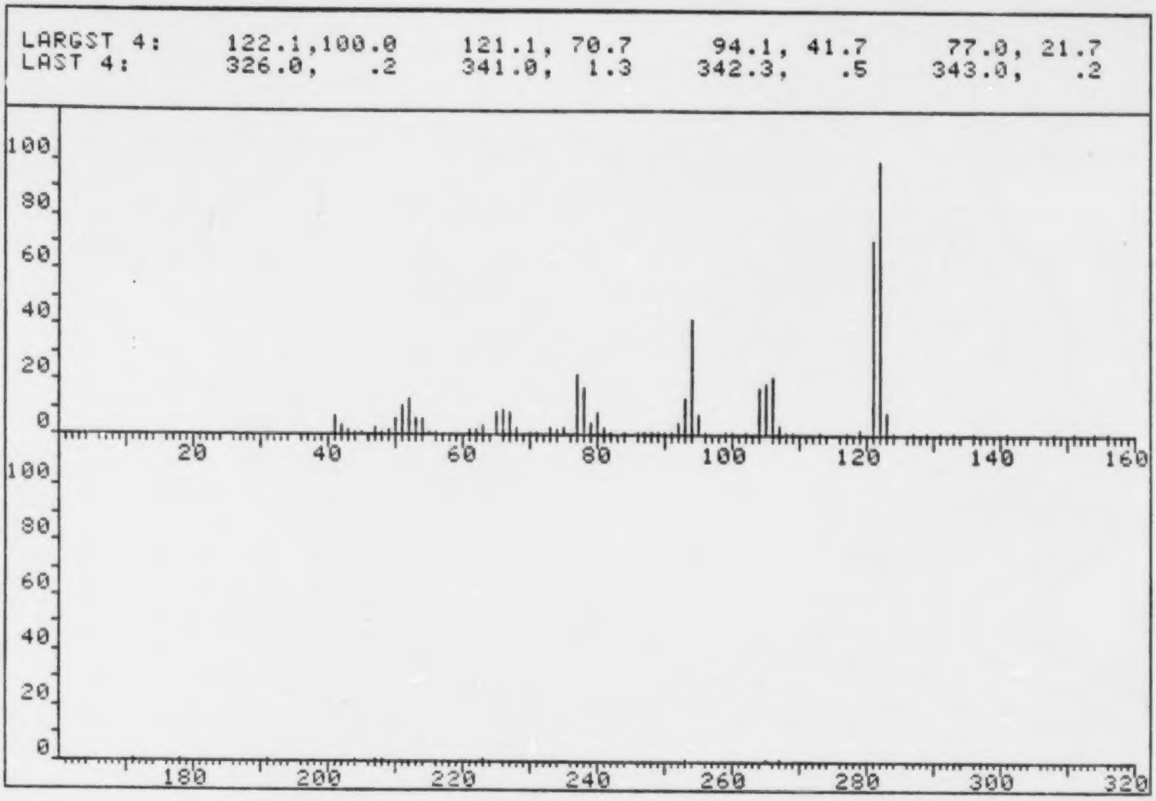


Figure B-34. Calibration curve for the determination of N-nitrosodibutylamine by GC/MS.

Range: 2.5 - 79 ng
Correlation coefficient: 0.998
Slope: 8.8×10^{-2}
y-Intercept: -3.0×10^{-1}



```
LARGST 4:     122.1,100.0     121.1, 70.7      94.1, 41.7      77.0, 21.7
LAST 4:       326.0,    .2    341.0,  1.3     342.3,   .5     343.0,    .2
```

Figure B-35. Mass spectrum for 3,4-diaminotoluene.

TABLE B-16. KEY IONS AND RELATIVE ABUNDANCES FOR 3,4-DIAMINOTOLUENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	6.2	74	1.3	105	18.8	178	.2
42	3.2	75	2.1	106	21.1		
43	1.4			107	3.3	191	.1
44	.1	77	21.7	108	.3		
45	.5	78	17.3	109	.2	204	.1
47	2.4	79	4.0	113	.1	207	.2
		80	8.3	117	.3	208	.2
48	.2	81	2.3				
49	1.4	82	.6	119	1.9	223	.2
50	5.4	84	.3	121	70.7		
51	10.6	86	.3	122	100.0	253	.2
52	12.6	87	.3	123	8.1		
53	6.1	88	.1	124	.6	265	.2
54	6.0	89	.6	127	.2	267	.1
55	1.1			129	.1		
56	.3	90	.4	131	.2	325	.5
61	1.5	91	1.2			326	.2
		92	4.5	133	.3		
62	2.0	93	13.3	136	.2	341	1.3
63	3.1	94	41.7	141	.2		
65	8.3	95	7.4			342	.5
66	8.8	96	.6	148	.3	343	.2
67	7.8	99	.1	151	.1		
68	2.7	100	.0	154	.1		
70	.1	102	.3	156	.1		
71	.2						
73	2.4	104	17.4	171	.2		

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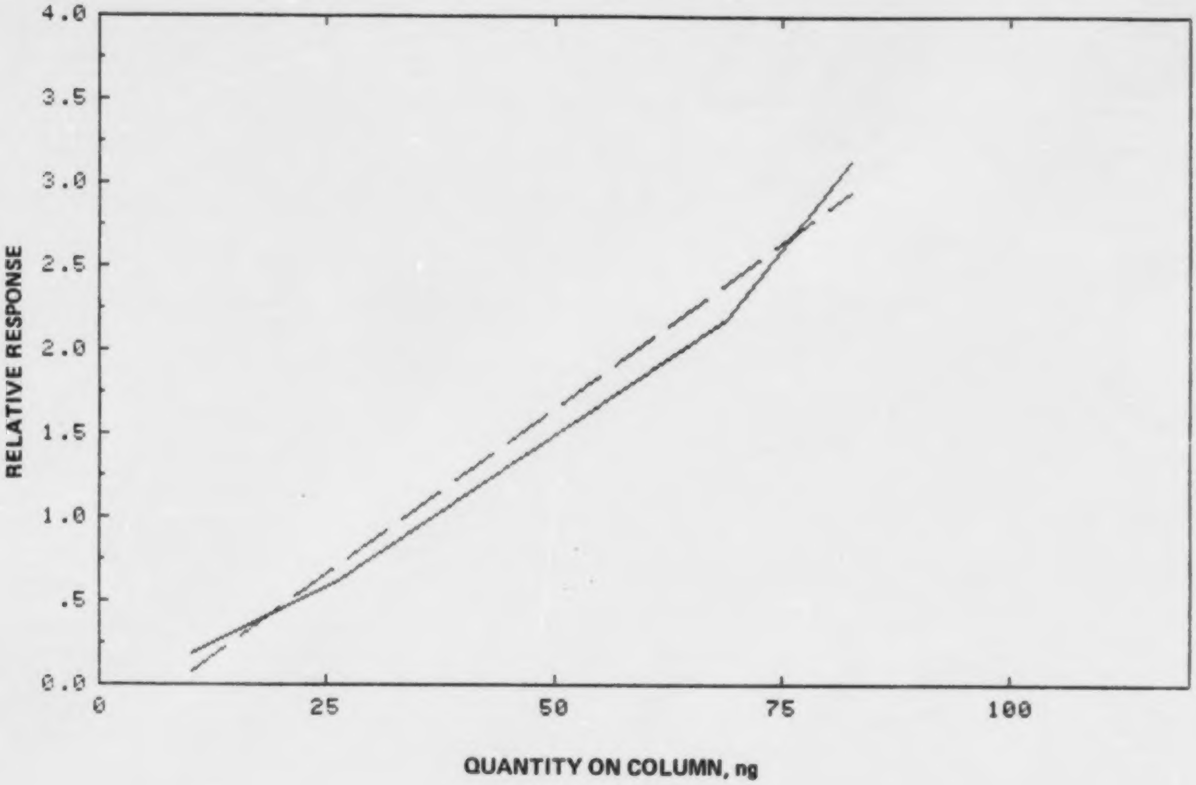
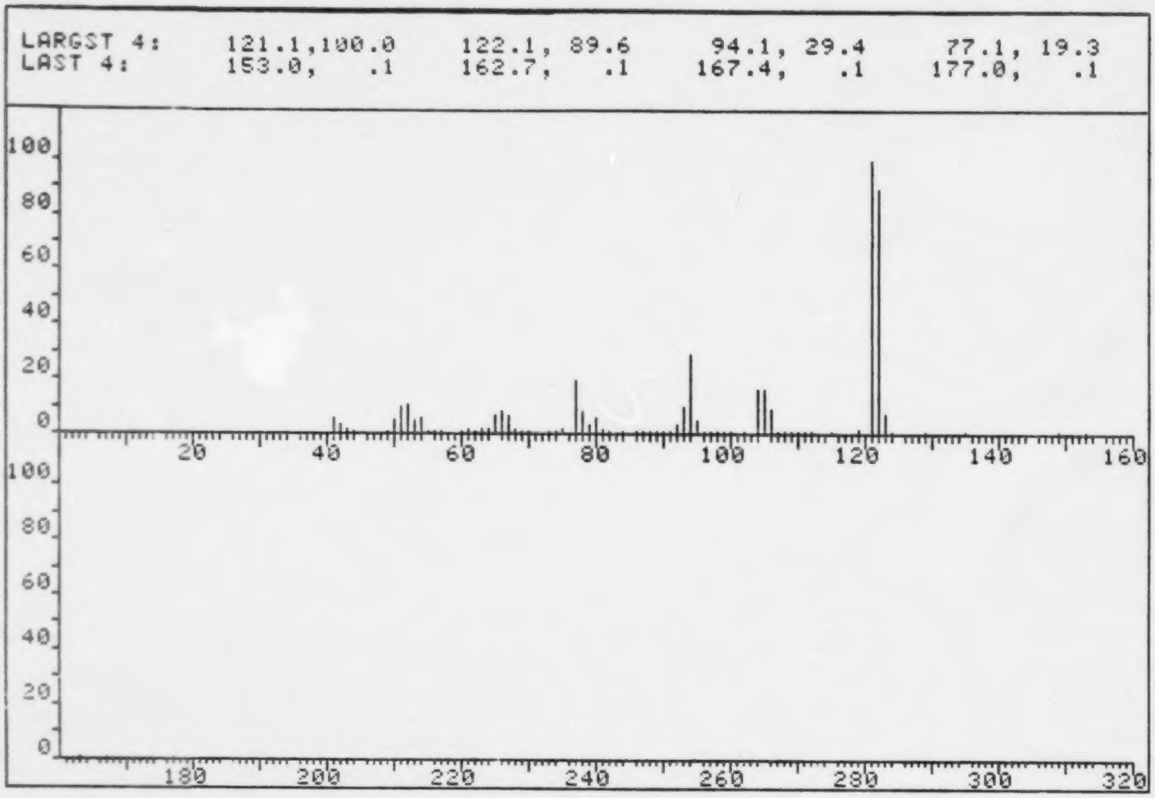


Figure B-36. Calibration curve for the determination of 3,4-diaminotoluene by GC/MS.

Range: 26 - 83 ng
Correlation coefficient: 0.992
Slope: 4.0×10^{-2}
y-Intercept: -3.3×10^{-1}



```
LARGST 4:     121.1,100.0     122.1, 89.6      94.1, 29.4      77.1, 19.3
LAST 4:       153.0,    .1    162.7,    .1    167.4,    .1    177.0,    .1
```

Figure B-37. Mass spectrum for 2,4-diaminotoluene.

TABLE B-17. KEY IONS AND RELATIVE ABUNDANCES FOR 2,4-DIAMINOTOLUENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	5.7	74	1.0	104	16.1	177	.1
42	3.3	75	1.6	105	15.9		
43	1.7			106	9.3		
44	.7	77	19.3	107	1.1		
		78	8.1	108	.1		
49	1.3	79	2.8	109	.1		
50	4.7	80	6.0	110	.1		
51	9.5	81	1.9	111	.1		
52	10.3	82	.7	112	.1		
53	5.3	84	.3	115	.1		
54	5.8	86	.4				
55	1.2	87	.2	119	1.7		
56	.6	88	.2	121	100.0		
57	.0	89	.3	122	89.6		
60	.8			123	7.5		
61	1.5	90	.5	124	.3		
		91	.7	129	.1		
62	1.2	92	2.8				
63	1.9	93	9.6	135	.1		
64	1.8	94	29.4	136	.1		
65	6.5	95	4.9				
66	8.0	96	.6	149	.0		
67	6.4	97	.2	153	.1		
68	1.5	98	.1				
69	.3	99	.2	163	.1		
70	.2	100	.0	167	.1		
73	.3	102	.6				

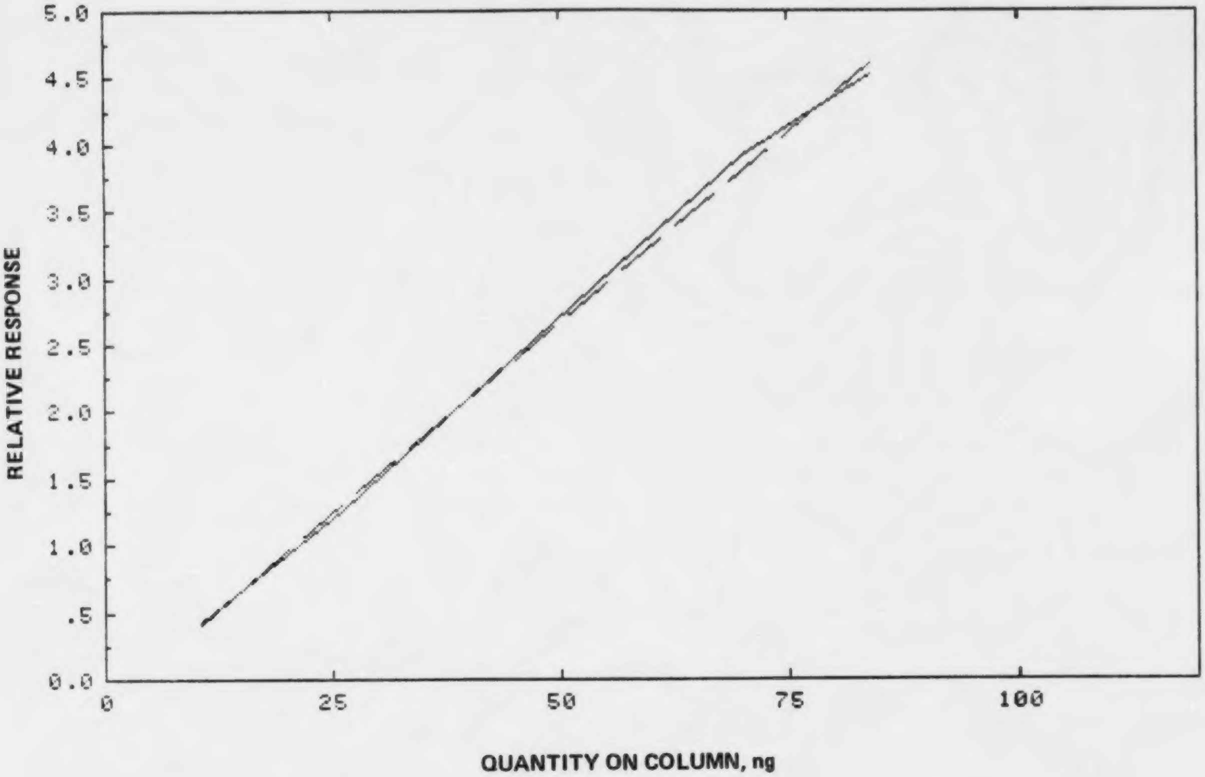
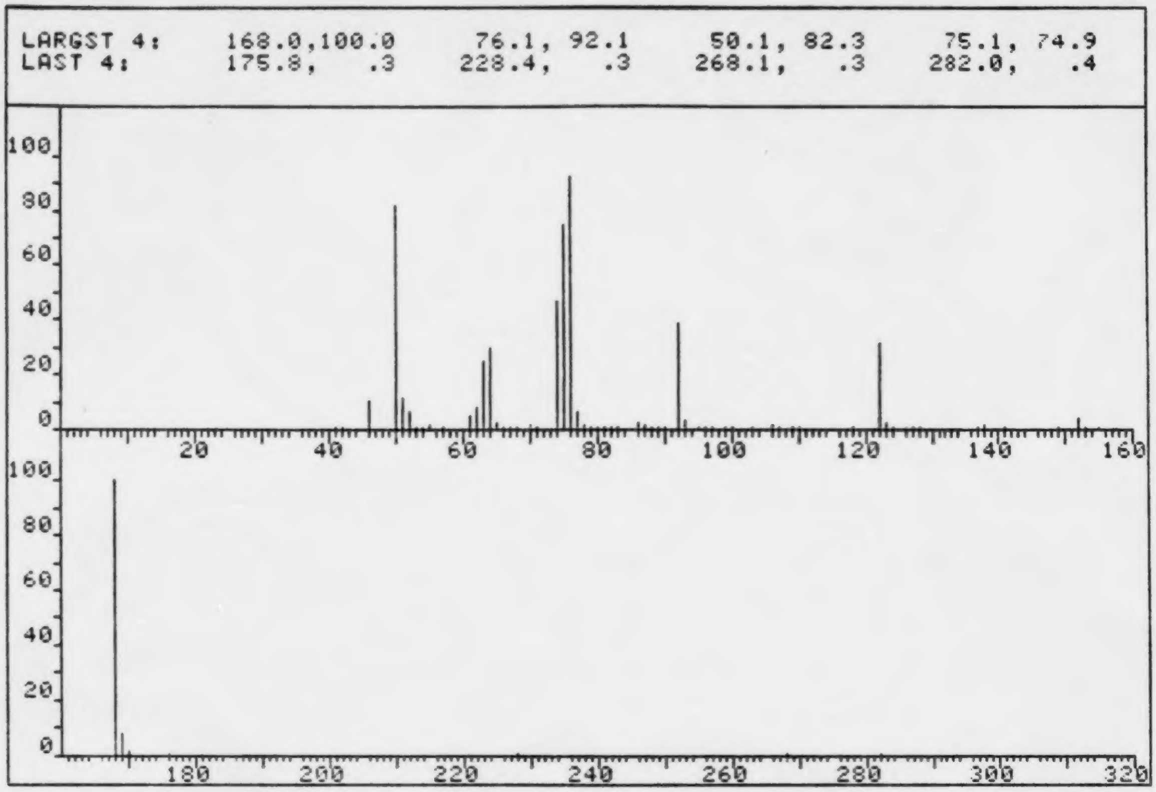


Figure B-38. Calibration curve for the determination of 2,4-diaminotoluene by GC/MS.

Range: 10 - 84 ng
Correlation coefficient: 0.999
Slope: 5.7×10^{-2}
y-Intercept: -1.8×10^{-1}



```
LARGST 4:     168.0,100.0     76.1, 92.1     50.1, 82.3     75.1, 74.9
LAST 4:       175.8,    .3   228.4,   .3    268.1,   .3    282.0,   .4
```

Figure B-39. Mass spectrum for m-dinitrobenzene.

TABLE B-18. KEY IONS AND RELATIVE ABUNDANCES OF _m_-DINITROBENZENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	.2	78	1.6	122	32.0
42	.3	79	1.3	123	2.7
46	10.3	80	1.2	124	.4
		81	.5	126	.3
50	82.3	82	.6	127	.2
51	10.9	83	.8	128	.3
52	6.7	86	2.2		
53	1.1	87	1.6	137	.4
54	.3	88	.5	138	1.9
55	1.7	89	.5	141	.3
57	.8				
61	5.0	90	.5	149	.1
		92	38.4	152	4.1
62	8.6	93	3.7	153	.3
63	24.7	95	.3	155	.5
64	30.2	96	.1		
65	2.4	97	.3	168	100.0
66	1.0	99	.4	169	8.2
67	.7	100	.4	170	1.2
68	.1	103	.4		
70	1.6			176	.3
71	.1	106	1.7		
74	46.6	107	.8	228	.3
75	74.9	109	.5		
		110	.4	268	.3
76	92.1				
77	6.1	118	.5	282	.4

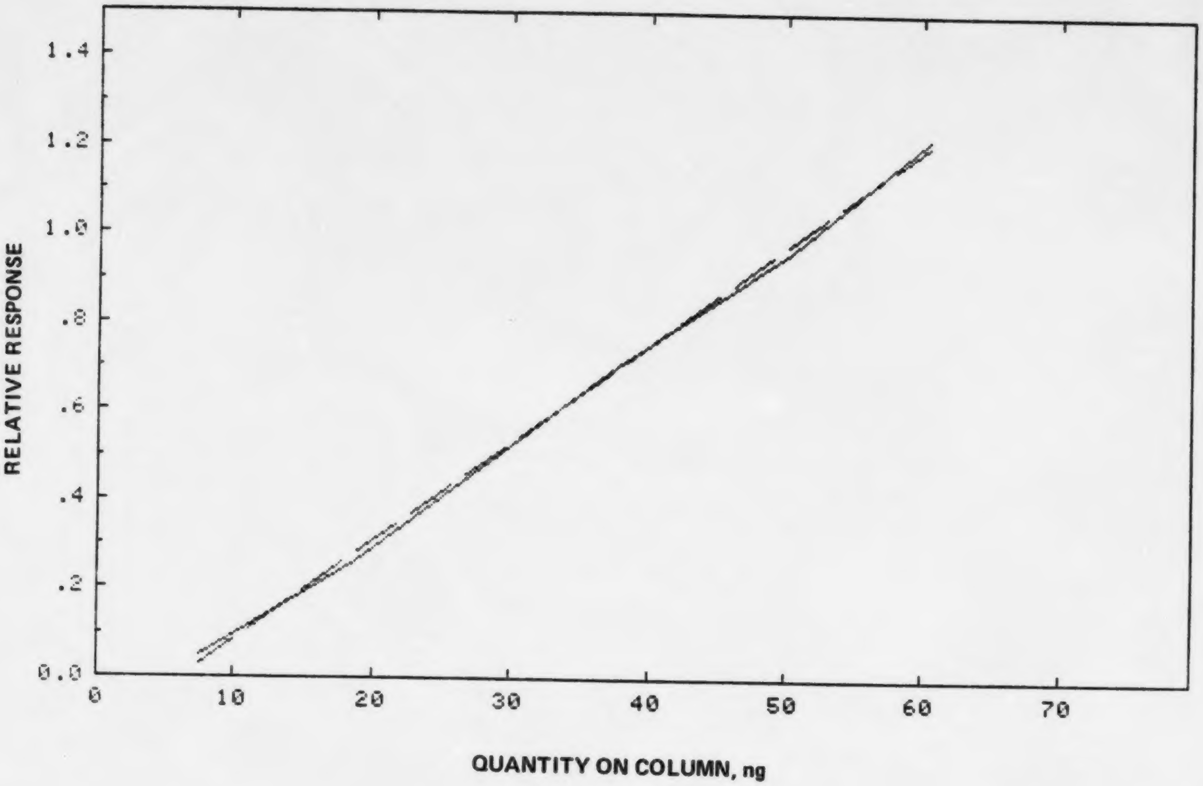


Figure B-40. Calibration curve for the determination of m-dinitrobenzene by GC/MS.

Range: 19 - 60 ng
Correlation coefficient: 0.999
Slope: 2.2×10^{-2}
y-Intercept: -1.4×10^{-1}

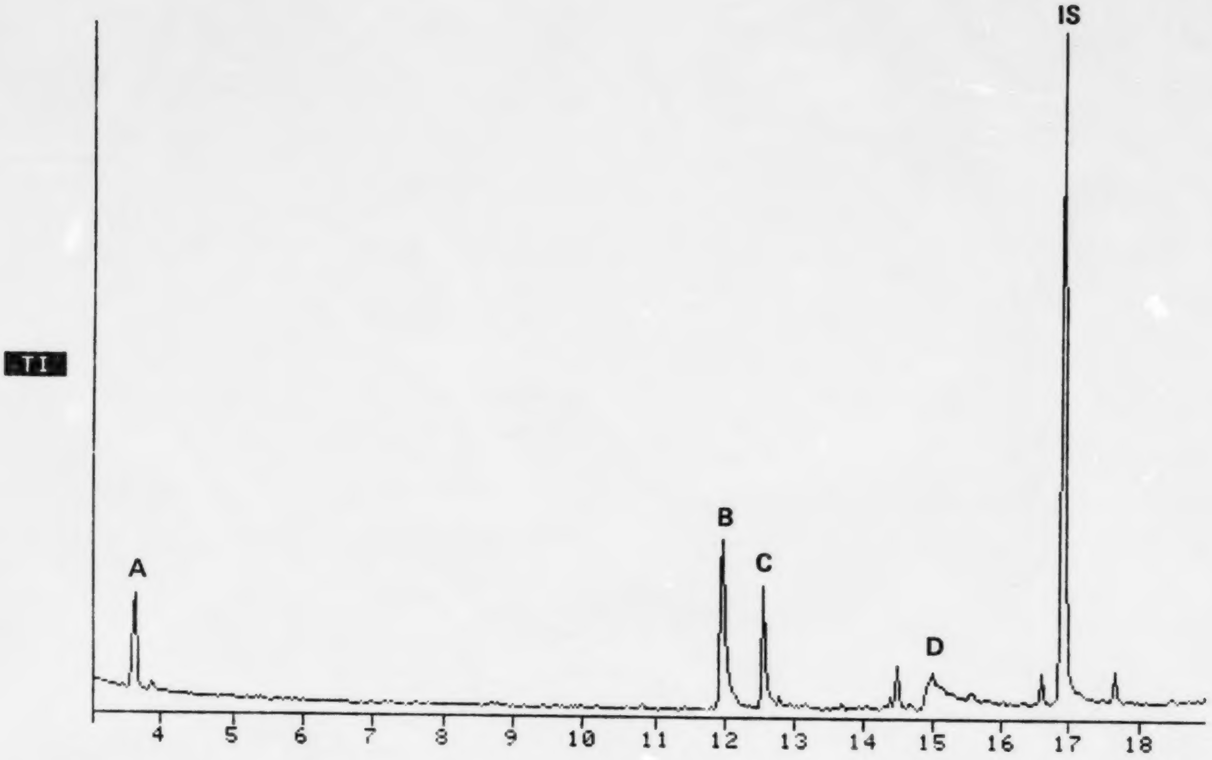


Figure B-41. Chromatogram by GC/MS for

(A) N-nitroso-N-methylethylamine(t_R = 3.7 min),
(B) 2,6-diaminotoluene(t_R = 11.9 min),
(C) p-dinitrobenzene(t_R = 12.6 min),
(D) p-nitroaniline(t_R = 15.0 min), and
malononitrile(not shown).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

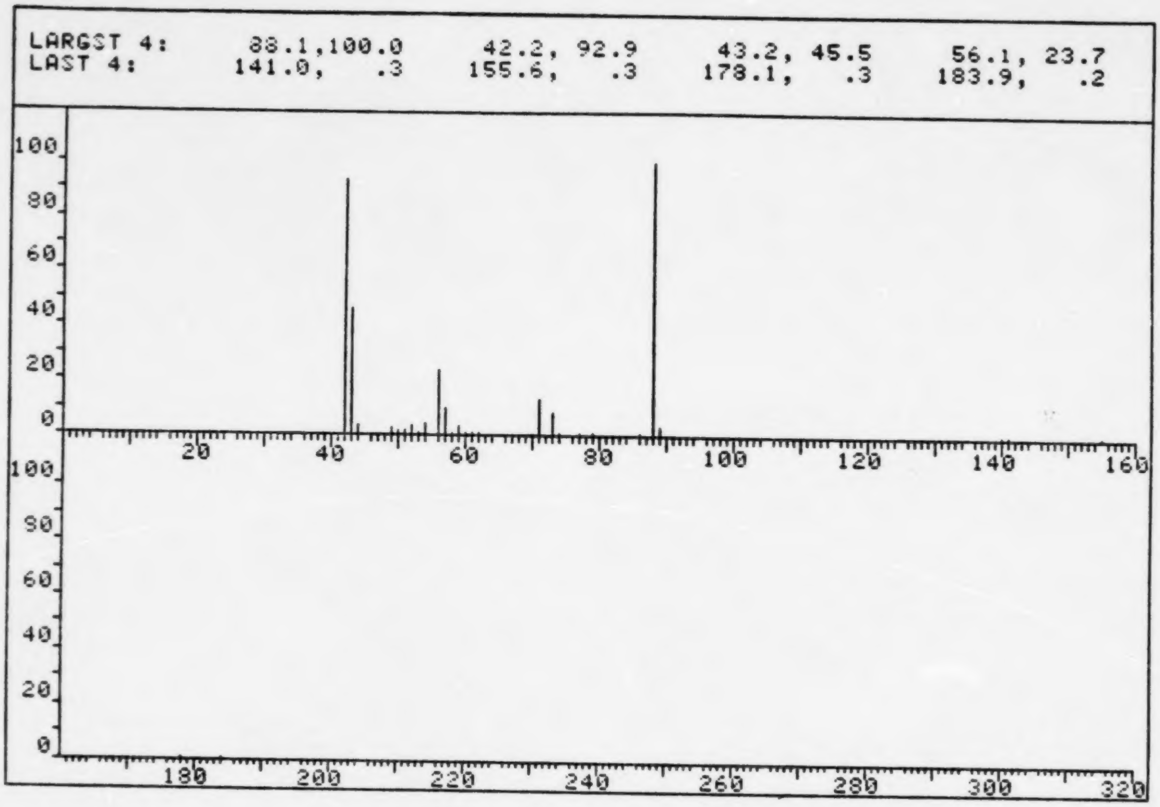


Figure B-42. Mass spectrum for N-nitroso-N-methylethylamine.

TABLE B-19. KEY IONS AND RELATIVE ABUNDANCES FOR *N*-NITROSO-*N*-METHYLETHYLAMINE

M/Z	Abundance	M/Z	Abundance
42	92.9	140	.3
43	45.5	141	.3
44	3.7		
		155	.3
49	2.2		
50	2.0	178	.3
51	1.4	184	.2
52	3.8		
53	1.0		
54	4.4		
56	23.7		
57	9.8		
58	.7		
59	3.3		
60	.6		
61	.5		
62	.4		
71	13.4		
73	8.1		
74	.5		
77	.1		
79	.3		
86	.3		
88	100.0		
89	3.7		

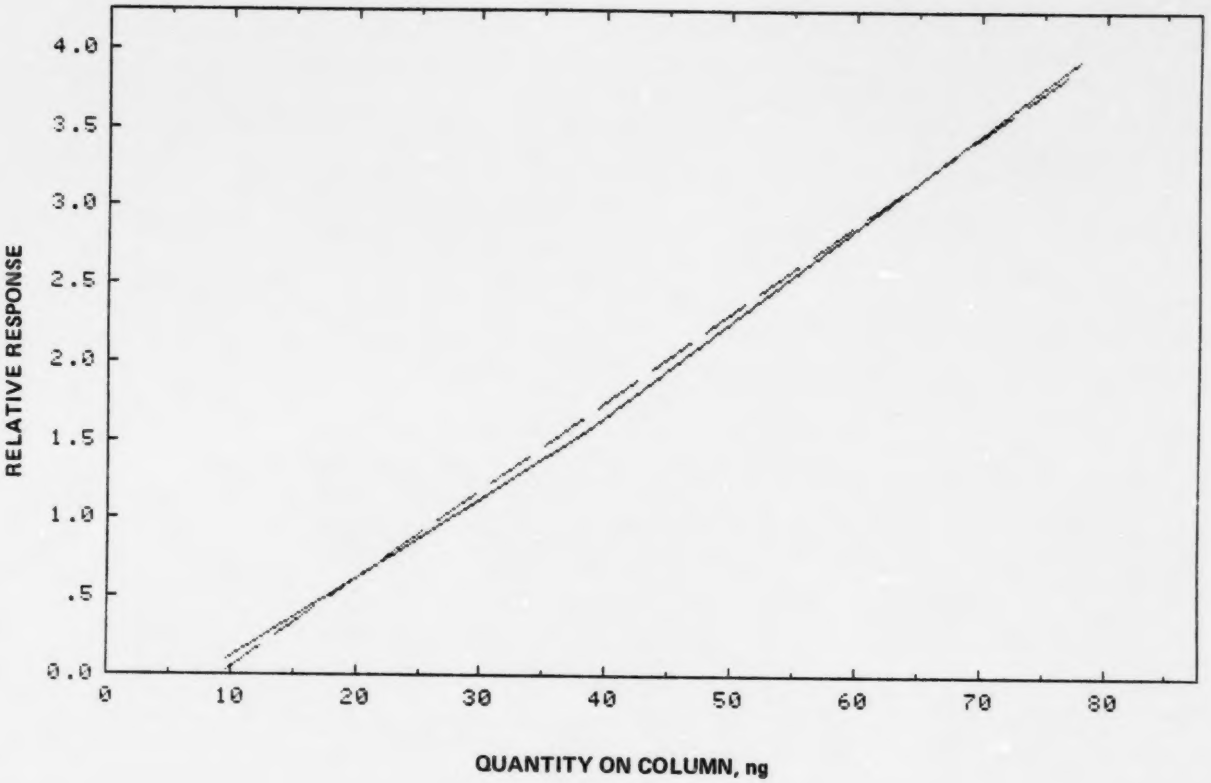


Figure B-43. Calibration curve for the determination of N-nitroso-N-methylethylamine by GC/MS.

Range: 24 - 78 ng
Correlation coefficient: 0.999
Slope: 5.7×10^{-2}
y-Intercept: -5.2×10^{-1}

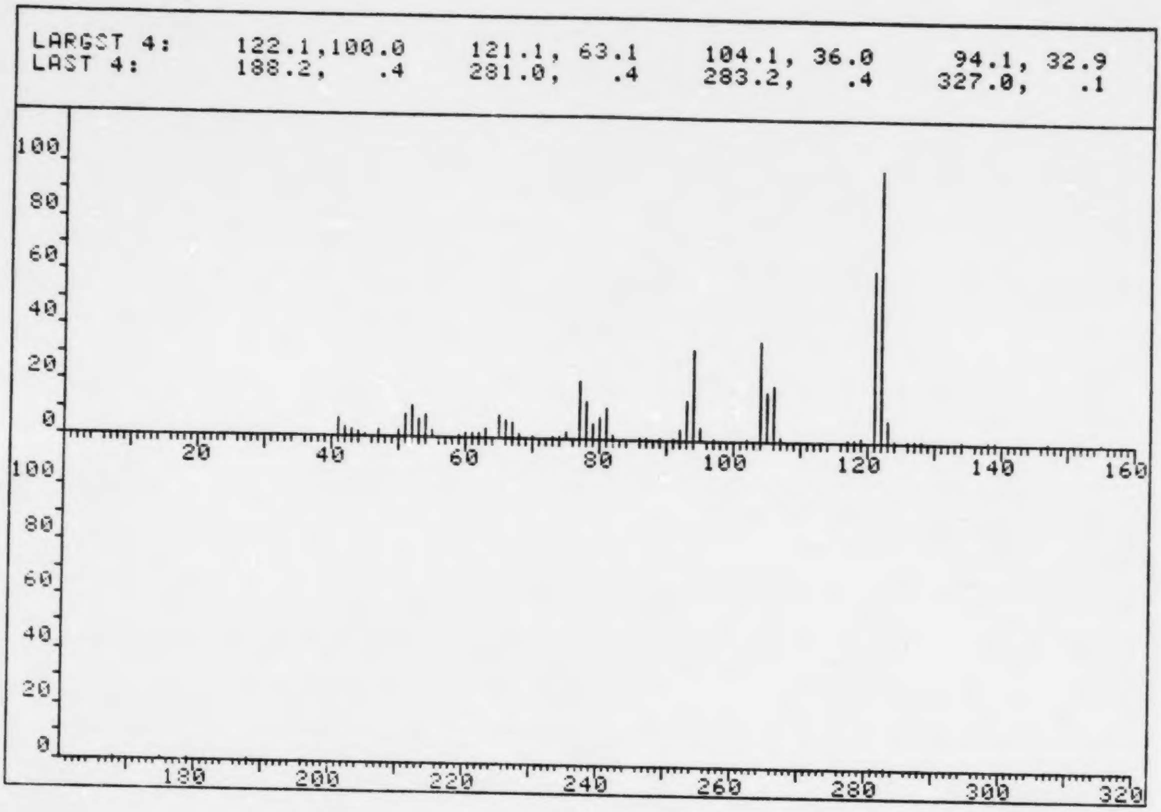


Figure B-44. Mass spectrum for 2,6-diaminotoluene.

TABLE B-20. KEY IONS AND RELATIVE ABUNDANCES FOR 2,6-DIAMINOTOLUENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	6.6	75	2.2	119	2.0
42	3.2			121	63.1
43	2.1	77	21.0	122	100.0
44	1.8	78	14.2	123	8.3
45	1.0	79	5.8	124	.4
45	.8	80	7.7	126	.4
47	2.1	81	11.4	127	.1
		82	1.5	128	.3
50	2.5	86	.2		
51	8.6	87	.5	134	.3
52	11.6	89	.7	138	.3
53	6.4			139	.3
54	8.1	91	.8		
55	2.3	92	4.0	147	.7
59	.7	93	14.7	155	.4
60	1.8	94	32.9		
61	1.7	95	4.8	168	.4
		97	.4		
62	1.6	102	1.0	175	.3
63	2.9			179	.4
65	8.4	104	36.0		
66	6.4	105	18.0	188	.4
67	5.7	106	19.9		
68	1.8	107	1.5	281	.4
70	.7	117	.4	283	.4
73	.6				
74	1.0	118	.9	327	.1

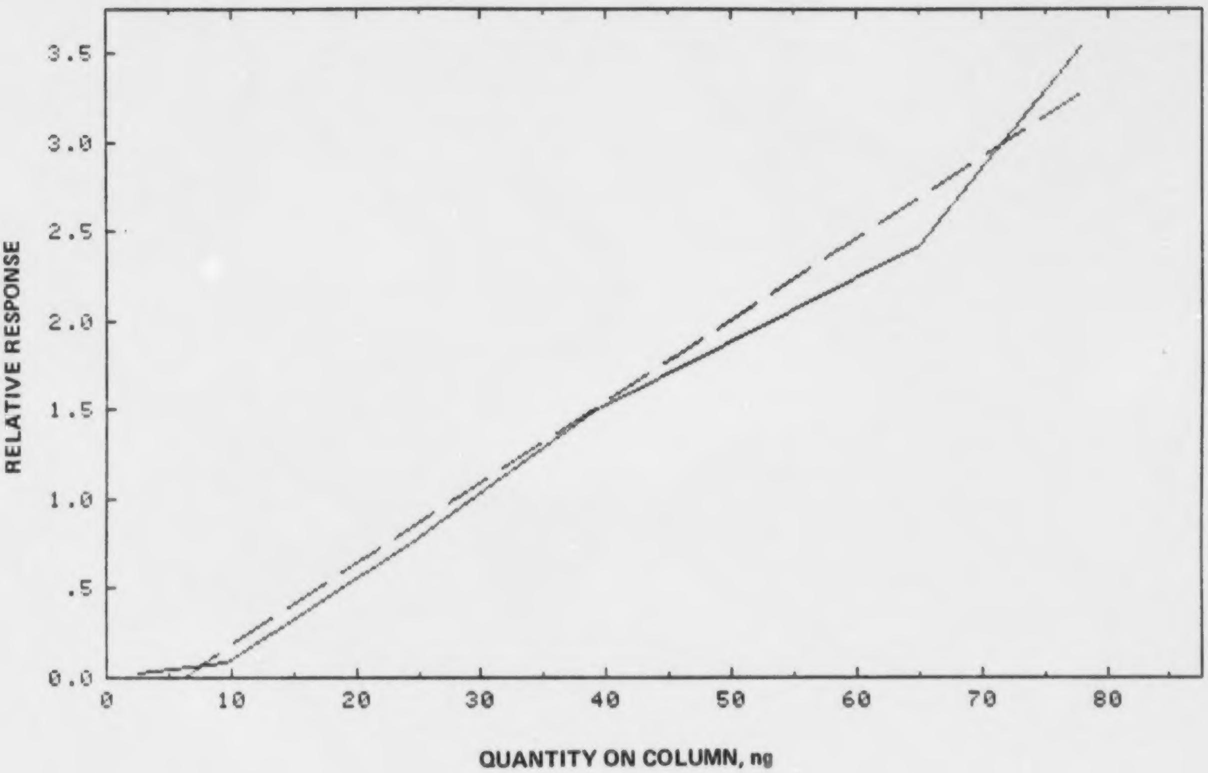


Figure B-45. Calibration curve for the determination of 2,6-diaminotoluene by GC/MS.

Range: 24 - 78 ng
Correlation coefficient: 0.990
Slope: 4.6×10^{-2}
y-Intercept: -2.8×10^{-1}

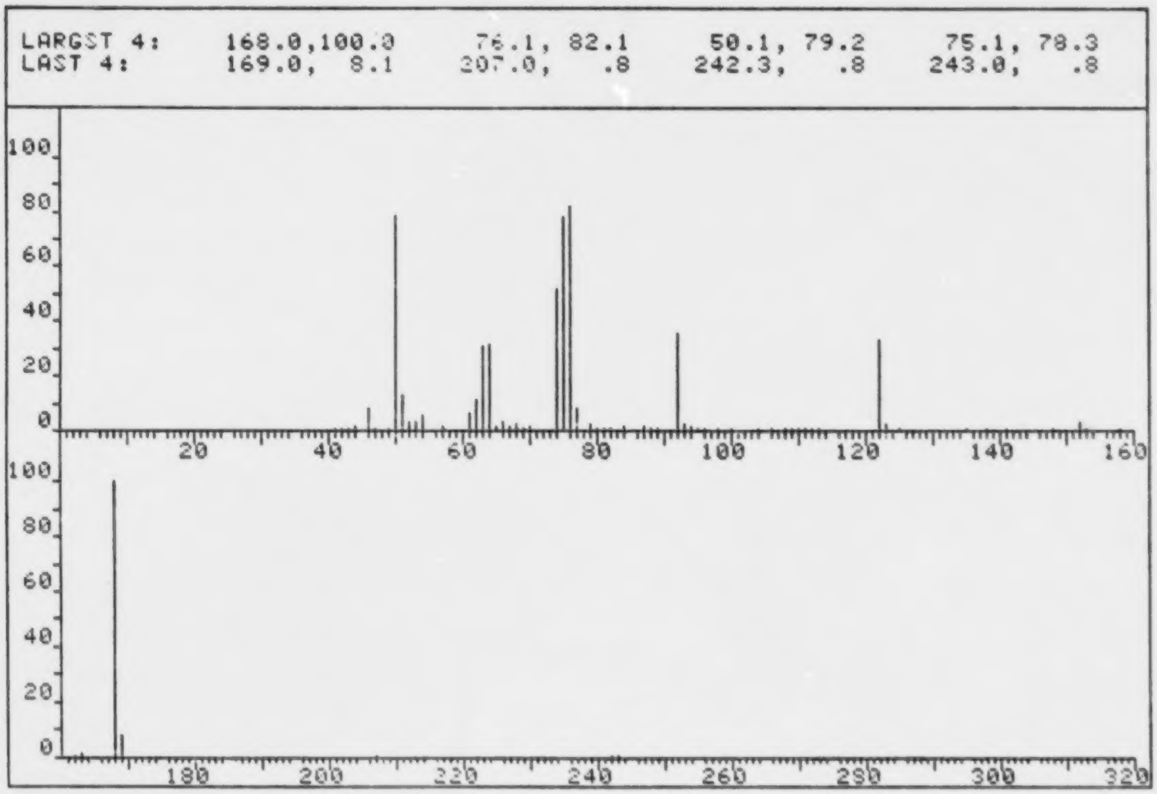

```
LARGST 4:     168.0,100.0      76.1, 82.1      50.1, 79.2      75.1, 78.3
LAST 4:       169.0,  8.1     207.0,   .8     242.3,   .8     243.0,   .8
```

Figure B-46. Mass spectrum for p-dinitrobenzene.

TABLE B-21. KEY IONS AND RELATIVE ABUNDANCES FOR *p*-DINITROBENZENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	1.3	76	82.1	122	33.5
42	.3	77	8.4	123	2.7
43	.5	79	2.4	125	1.0
44	1.6	80	1.3		
46	8.6	81	.5	135	.3
47	.3	82	.6	138	1.3
		84	1.4	141	.6
49	.6	87	1.6		
50	79.2	88	.8	148	1.3
51	12.5	89	1.0	152	3.0
52	3.3			153	.3
53	3.5	92	35.1	158	.8
54	5.4	93	2.2		
57	1.9	94	1.4	162	.8
61	6.8	95	.2	163	1.0
		96	.8	168	100.0
62	11.0	98	.8	169	8.1
63	30.3	100	1.0		
64	31.3			207	.8
65	1.7	104	1.0		
66	3.2	106	1.0	242	.8
67	1.6	108	.8	243	.8
68	2.1	109	1.3		
69	.8	110	1.0		
70	1.4	111	.3		
74	51.4	112	1.0		
75	78.3	113	1.1		

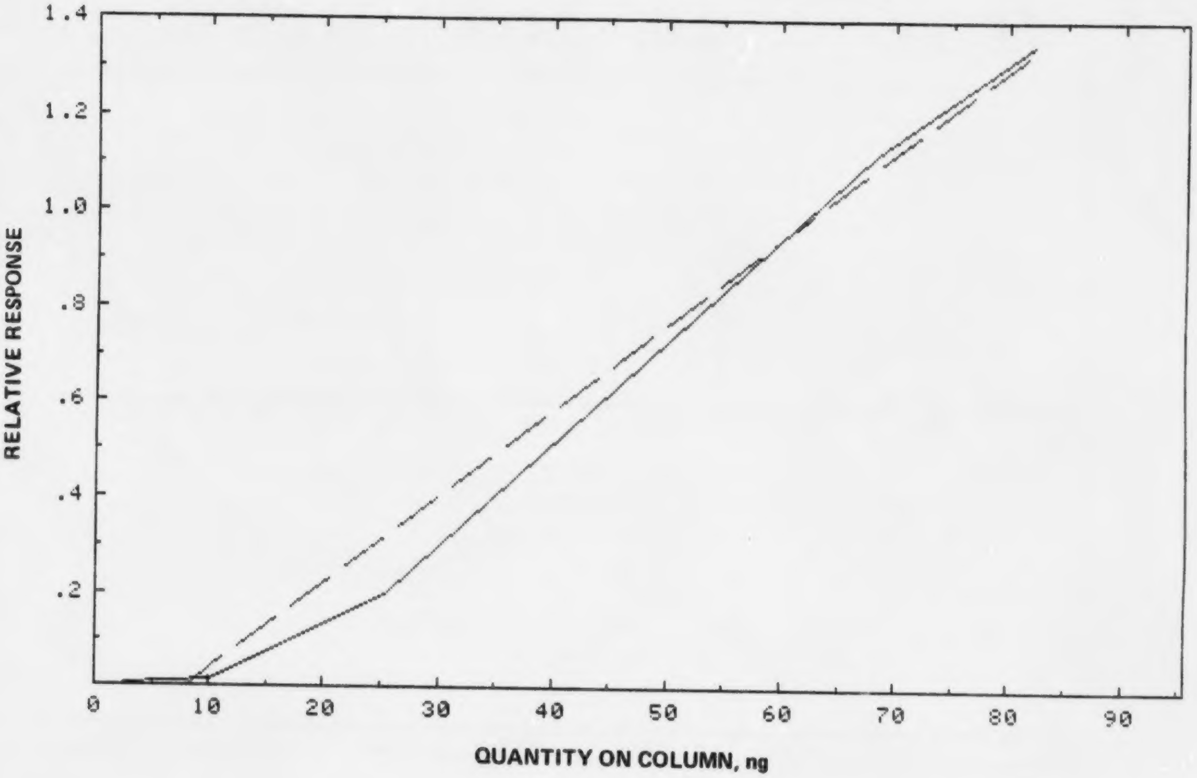
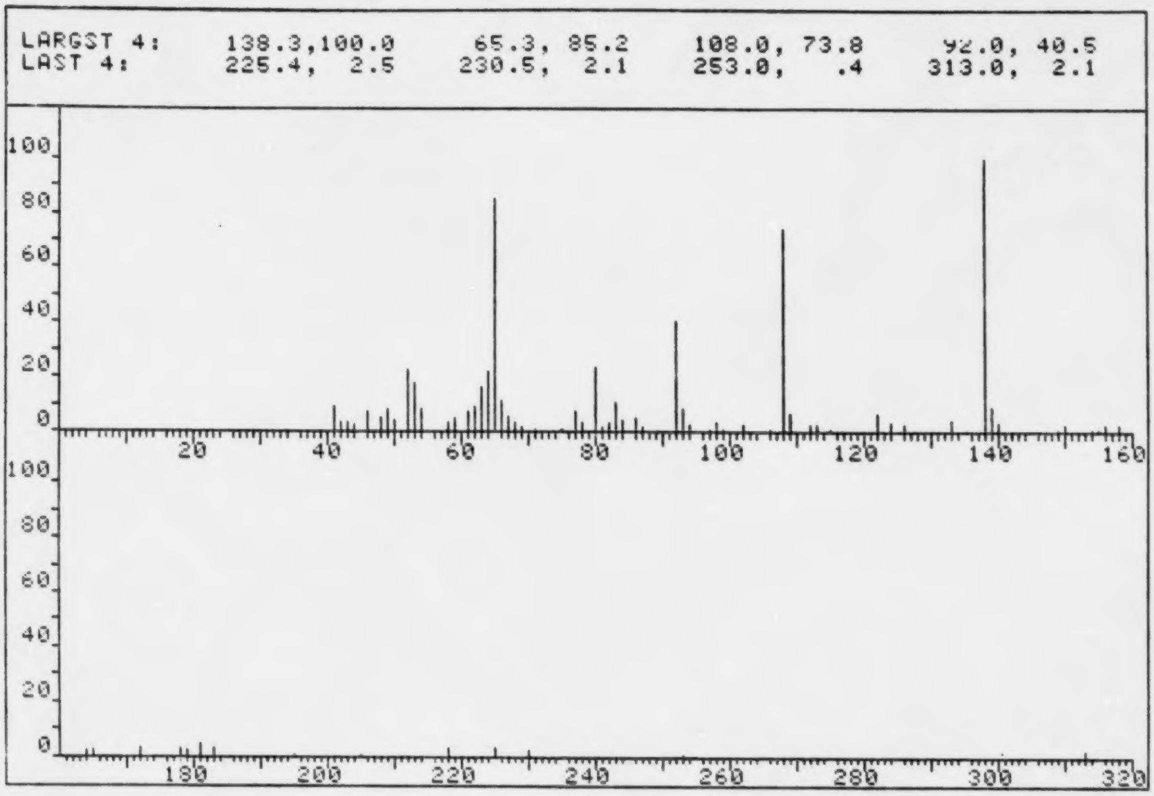


Figure B-47. **Calibration curve for the determination of _p_-dinitrobenzene by GC/MS.**

Range: 26 - 82 ng
Correlation coefficient: 0.992
Slope: 1.8×10^{-2}
y-Intercept: -1.4×10^{-1}



```
LARGST 4:     138.3,100.0      65.3, 85.2     108.0, 73.8      92.0, 40.5
LAST 4:       225.4,  2.5     230.5,  2.1     253.0,   .4     313.0,  2.1
```

Figure B-48. Mass spectrum for p-nitroaniline.

TABLE B-22. KEY IONS AND RELATIVE ABUNDANCES FOR *p*-NITROANILINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	8.9	77	7.2	124	3.0	218	3.0
42	3.8	78	3.4	126	2.1	225	2.5
43	3.4	80	23.6				
44	2.1	81	1.7	133	4.2	230	2.1
46	7.2	82	3.0	138	100.0		
		83	10.5	139	8.9	253	.4
48	4.6	84	4.2	140	3.8		
49	7.6	86	4.6			313	2.1
50	4.2	87	1.7	149	.4		
52	22.8			150	2.1		
53	18.1	92	40.5	154	.4		
54	8.4	93	8.0	155	.4		
58	3.4	94	2.5	156	2.1		
59	4.6	94	2.5	158	2.5		
61	7.2	97	.8				
		98	3.4	164	2.1		
62	8.9	99	.4	165	2.1		
63	16.5	102	2.5	172	2.5		
64	21.5						
65	85.2	106	.8	178	3.4		
66	11.0	108	73.8	179	2.1		
67	5.5	109	6.7	181	4.6		
68	3.4	112	2.5	183	3.0		
69	1.7	113	2.1				
71	.4	115	1.3	195	.4		
75	.4						
		122	6.3	205	.4		

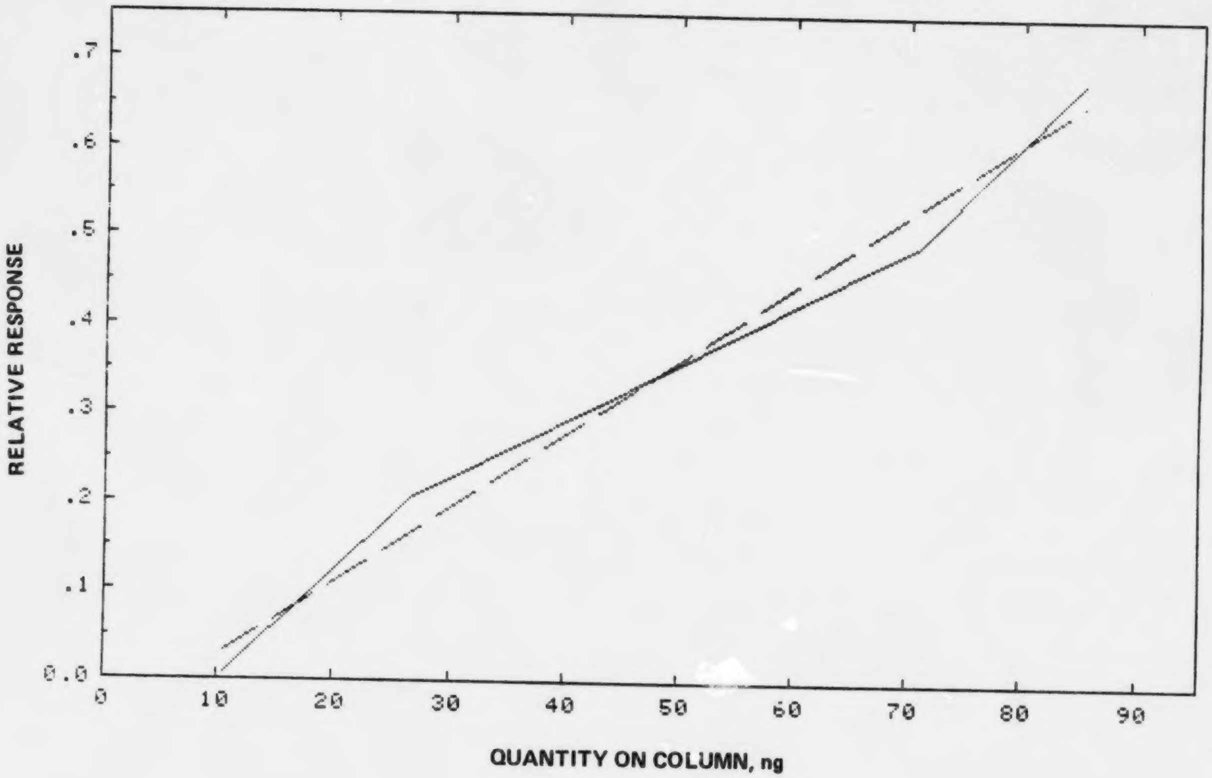
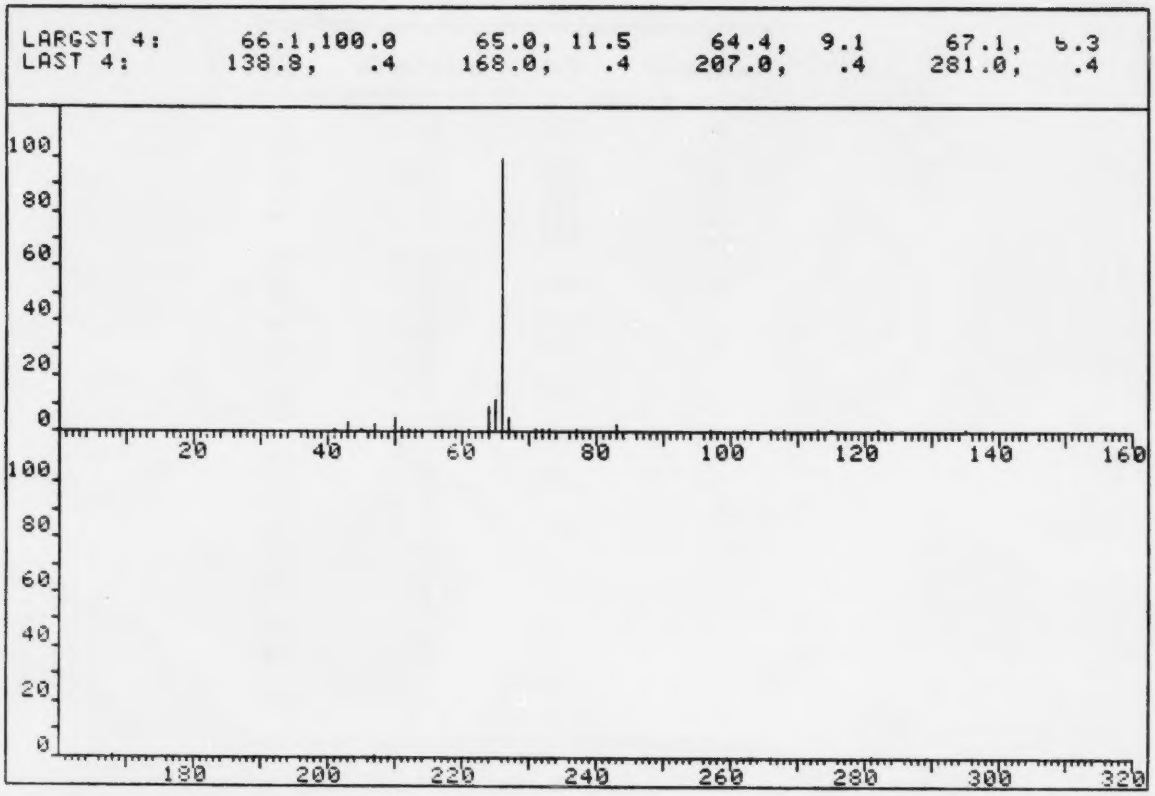


Figure B-49. Calibration curve for the determination of p-nitroaniline by GC/MS.

Range: 10 - 90 ng
Correlation coefficient: 0.991
Slope: 8.3 X 10^{-3}
y-Intercept: -5.6 X 10^{-2}



```
LARGST 4:     66.1,100.0      65.0, 11.5      64.4,  9.1      67.1,  5.3
LAST 4:      138.8,    .4    168.0,    .4    207.0,    .4    281.0,    .4
```

Figure B-50. Mass spectrum for malononitrile.

TABLE B-23. KEY IONS AND RELATIVE ABUNDANCES FOR MALONONITRILE

M/Z	Abundance	M/Z	Abundance
41	.4	102	.4
43	.3		
43	2.9	106	.4
45	.4	108	.4
47	2.1	113	.4
		115	.4
50	4.6		
51	2.0	122	.4
52	1.3		
53	.5	135	.4
54	.2	139	.4
57	.8		
59	1.2	168	.4
61	.5		
		207	.4
64	9.1		
65	11.5	281	.4
66	100.0		
67	5.3		
71	.2		
72	.3		
73	.8		
77	.6		
83	2.8		
97	.4		

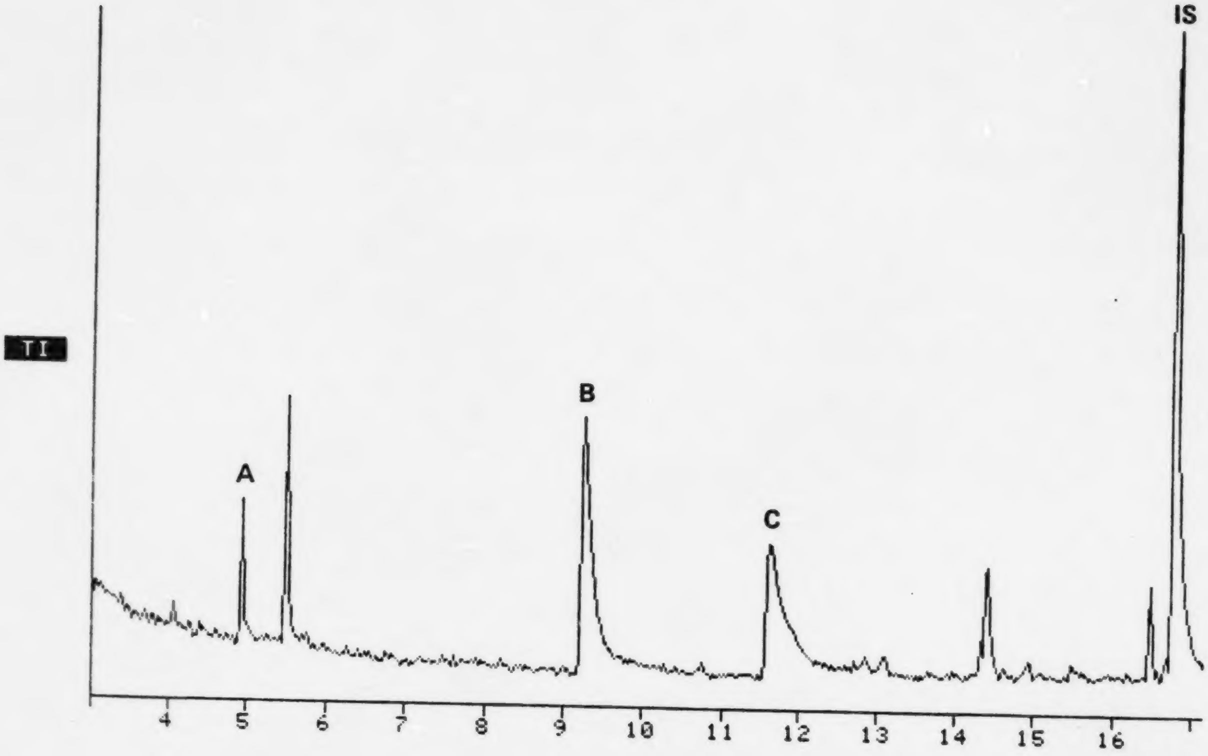
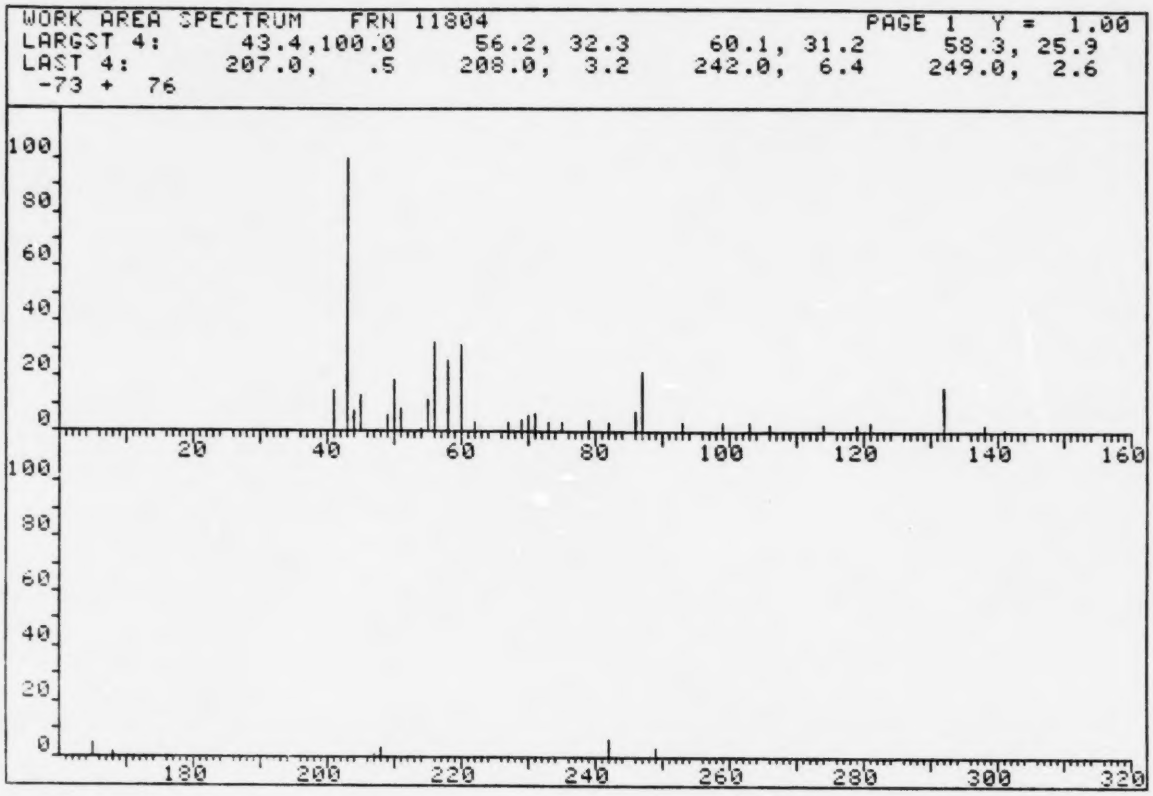


Figure B-51. Chromatogram by GC/MS for

(A) N-nitroso-N-methylurethane(t_R = 4.9 min),
(B) 2,6-dichlorophenol(t_R = 9.3 min), and
(C) 2,4,5-trichlorophenol(t_R = 11.7 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
WORK AREA SPECTRUM    FRN 11804                              PAGE 1   Y =  1.00
LARGST 4:      43.4,100.0       56.2, 32.3      60.1, 31.2      58.3, 25.9
LAST 4:       207.0,    .5     208.0,  3.2     242.0,  6.4     249.0,  2.6
 -73 +  76
```

Figure B-52. Mass spectrum for N-nitroso-N-methylurethane.

TABLE B-24. KEY IONS AND RELATIVE ABUNDANCES FOR *N*-NITROSO-*N*-METHYLURETHANE

M/Z	Abundance	M/Z	Abundance
41	14.8	93	3.2
43	100.0	99	3.7
44	6.9	103	3.7
45	12.7		
		106	2.6
49	5.8	114	2.6
50	19.0		
51	7.9	119	2.6
54	1.1	121	3.2
55	11.1		
56	32.3	132	16.4
58	25.9	138	2.1
60	31.2	141	.5
62	3.2	165	4.8
67	3.7	168	1.6
69	4.2		
70	5.8	207	.5
71	6.4	208	3.2
73	3.2		
75	3.7	242	6.4
79	4.2	249	2.6
82	3.2		
86	6.9		
87	21.7		

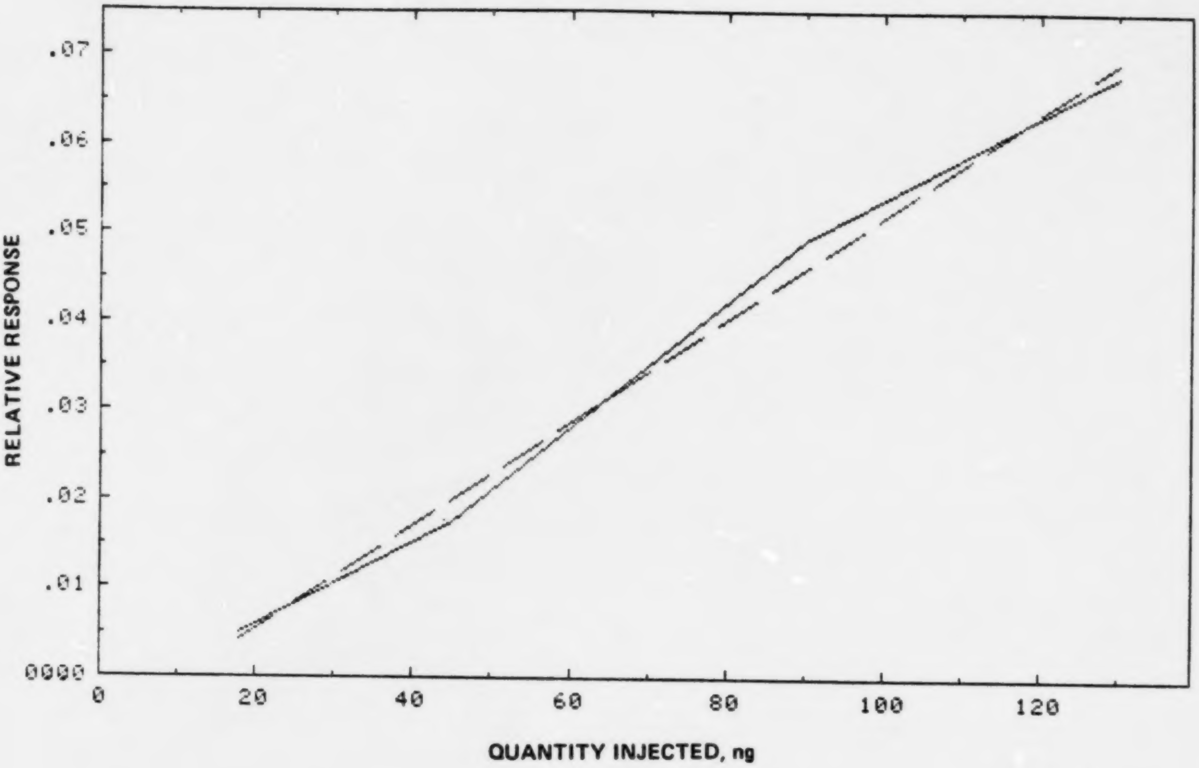
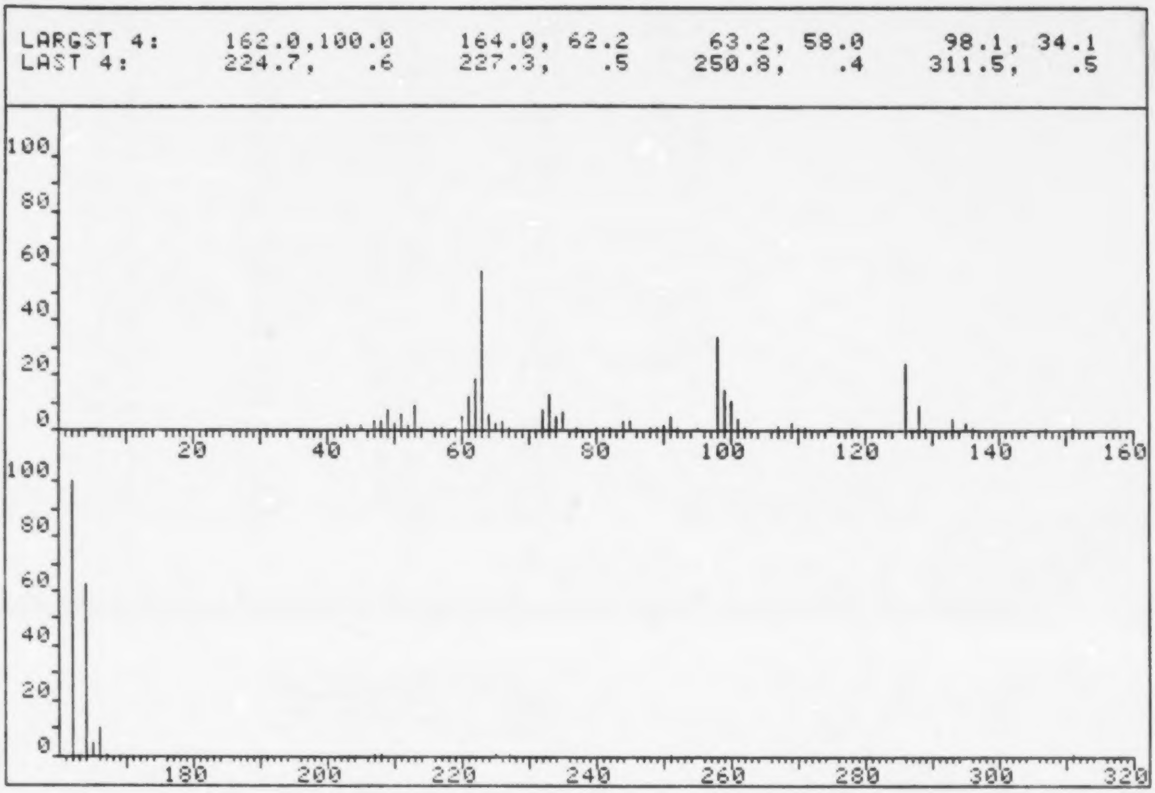


Figure B-53. Calibration curve for the determination of N-nitroso-N-methylurethane by GC/MS.

Range: 18 - 130 ng
Correlation coefficient: 0.996
Slope: 5.8 x 10^{-4}
y-Intercept: -6.2 x 10^{-3}



```
LARGST 4:    162.0,100.0    164.0, 62.2     63.2, 58.0     98.1, 34.1
LAST 4:      224.7,   .6    227.3,   .5    250.8,   .4    311.5,   .5
```

Figure B-54. Mass spectrum for 2,6-dichlorophenol.

TABLE B-25. KEY IONS AND RELATIVE ABUNDANCES FOR 2,6-DICHLOROPHENOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
42	1.2	75	6.3	118	.5	311	.5
43	1.9						
45	1.6	77	1.0	126	24.4		
47	3.6	80	.9	128	9.1		
		81	1.0	129	1.0		
48	3.4	82	1.2				
49	7.3	82	.6	133	4.2		
50	2.7	84	3.4	135	2.5		
51	6.0	85	3.3	136	.6		
52	1.7	88	.1	136	.5		
53	8.8	89	.9				
54	.6			147	1.2		
56	1.2	90	1.7	151	.5		
57	1.3	91	5.0				
59	1.2	92	.7	162	100.0		
60	4.8	95	.1	164	62.2		
61	12.3	98	34.1	165	4.6		
		99	14.9	166	10.1		
62	18.5	100	10.4	167	.7		
63	58.0	101	4.4				
64	5.5	102	.6	207	.9		
65	2.4			208	.5		
66	3.1	107	1.7				
67	.8	109	2.1	225	.6		
72	7.1	110	.8	227	.5		
73	13.0	111	.8				
74	4.9	115	.2	251	.4		

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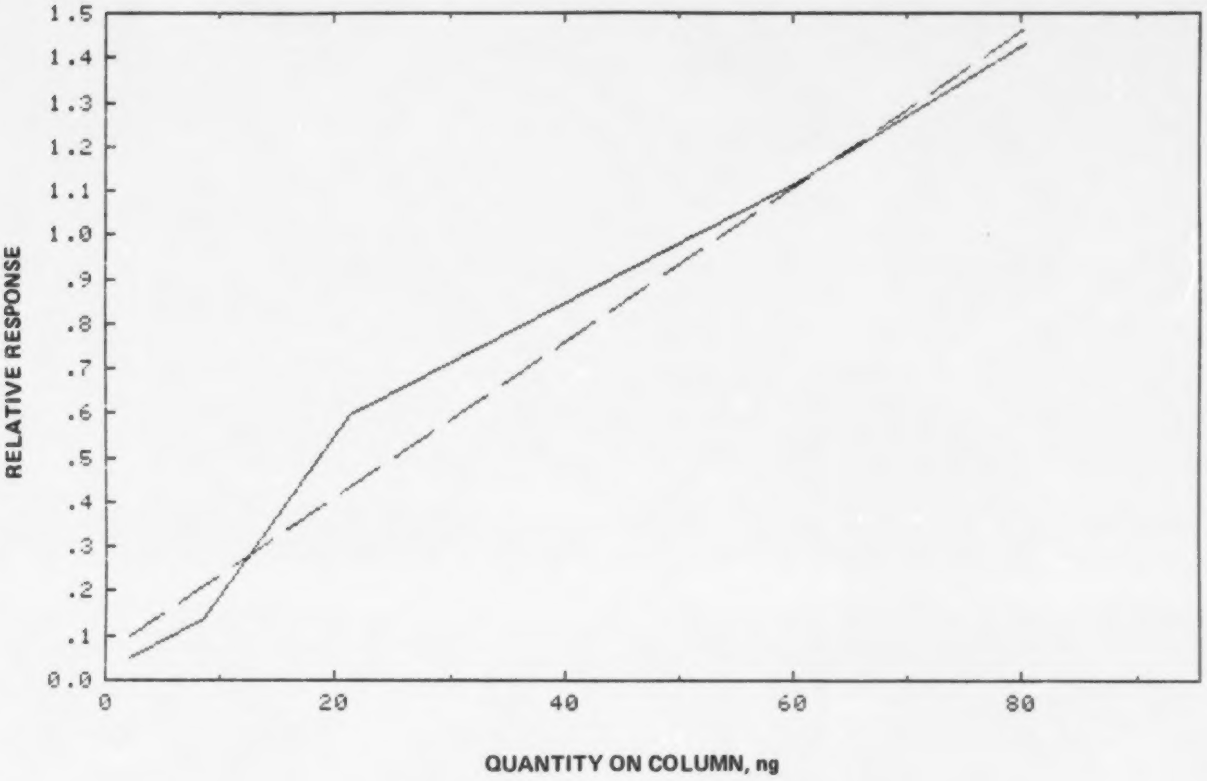
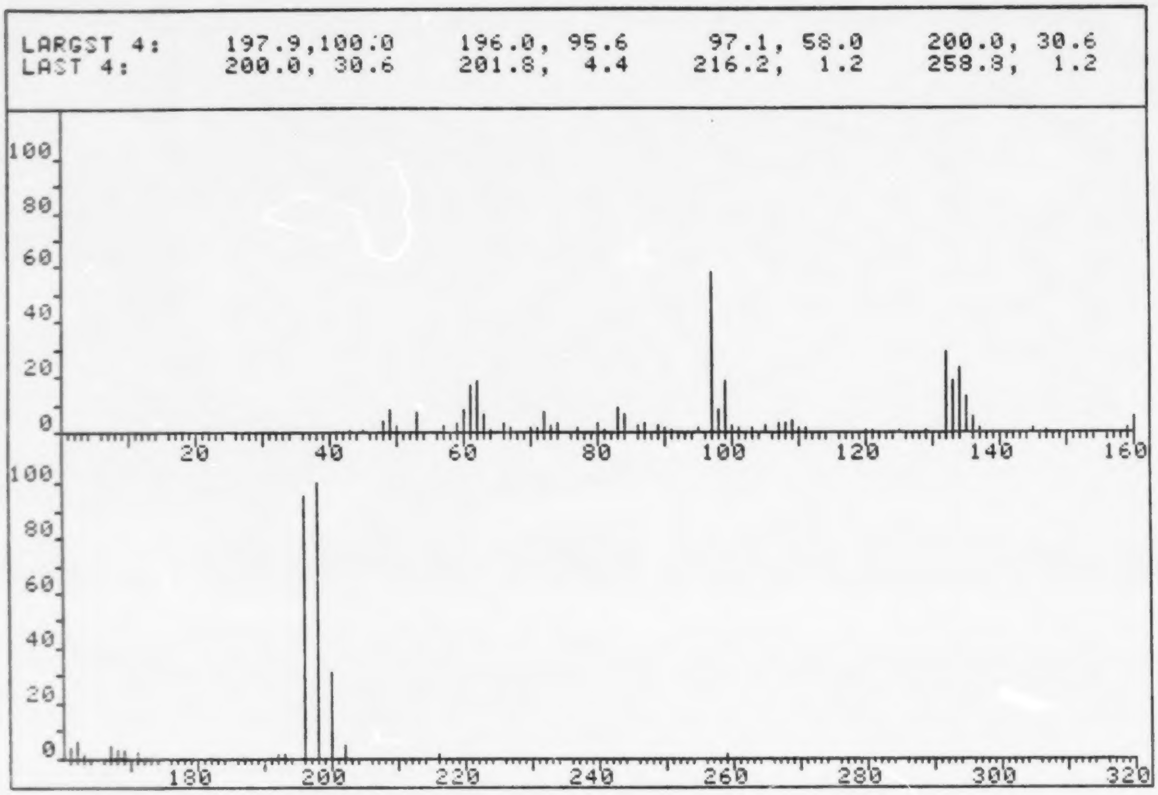


Figure B-55. Calibration curve for the determination of 2,6-dichlorophenol by GC/MS.

Range: 21 - 80 ng
Correlation coefficient: 0.987
Slope: 1.8×10^{-2}
y-Intercept: 6.2×10^{-2}



```
LARGST 4:     197.9,100.0     196.0, 95.6      97.1, 58.0     200.0, 30.6
LAST 4:       200.0, 30.6     201.8,  4.4     216.2,  1.2     258.8,  1.2
```

Figure B-56. Mass spectrum for 2,4,5-trichlorophenol.

TABLE B-26. KEY IONS AND RELATIVE ABUNDANCES FOR 2,4,5-TRICHLOROPHENOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43	.7	84	6.2	132	29.1	202	4.4
45	1.0	86	2.7	133	19.0		
		87	3.5	134	23.2	216	1.2
48	4.4	89	2.7	135	13.1		
49	8.1			136	5.4	259	1.2
50	2.2	90	1.7	137	1.7		
53	6.9	91	.7	145	1.7		
57	2.5	95	1.7	145	1.0		
59	3.7	97	58.0				
60	8.6	98	7.7	147	1.2		
61	16.8	99	19.0	159	1.7		
		100	2.7				
62	18.8	101	1.7	160	5.9		
63	6.2	103	1.5	161	3.9		
64	.5			162	6.4		
66	3.0	105	2.7	163	1.0		
67	1.5	107	3.7	167	4.7		
70	2.0	108	3.5	168	2.5		
71	1.5	109	4.4	169	3.5		
72	6.9	110	2.0	171	2.2		
73	2.5	111	1.7				
74	3.7			192	1.2		
		120	1.2	193	1.5		
77	2.0	121	1.2	196	95.6		
80	3.7	125	1.2	198	100.0		
81	1.0	129	.5	200	30.6		
83	9.1						

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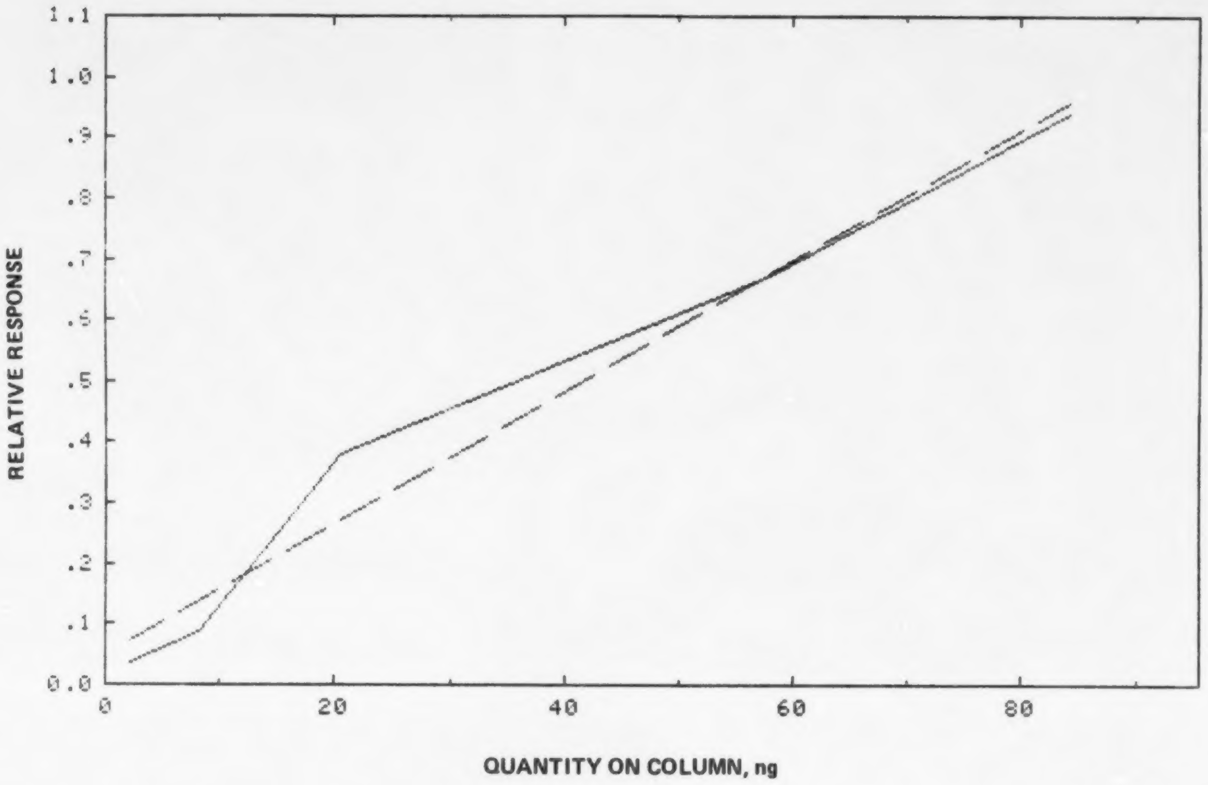


Figure B-57. Calibration curve for the determination of 2,4,5-trichlorophenol by GC/MS.

Range: 21 - 84 ng
Correlation coefficient: 0.986
Slope: 1.1×10^{-2}
y-Intercept: 4.9×10^{-2}

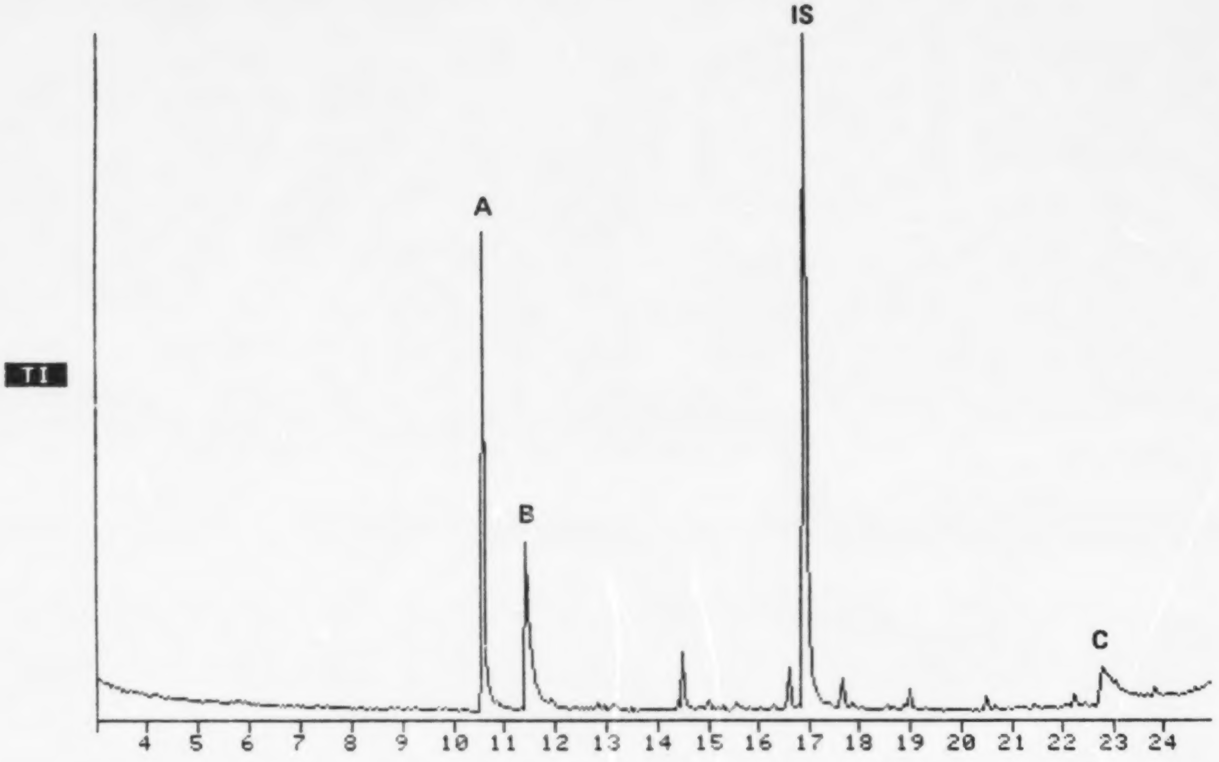
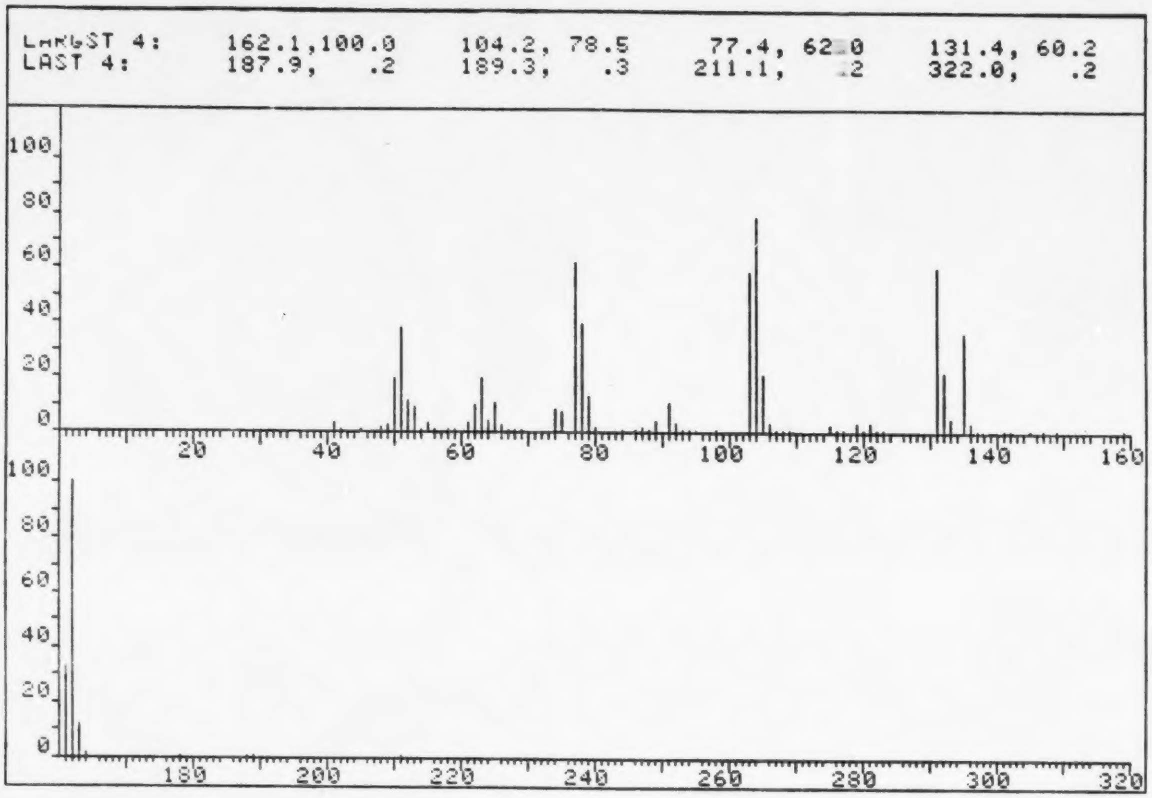


Figure B-58. Chromatogram by GC/MS for

(A) safrole(t_R = 10.6 min),
(B) nicotine(t_R = 11.4 min), and
(C) 2-acetamidofluorene(t_R = 22.8 min).

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:     162.1,100.0     104.2, 78.5       77.4, 62.0      131.4, 60.2
LAST 4:       187.9,    .2    189.3,    .3     211.1,    .2     322.0,    .2
```

Figure B-59. Mass spectrum for safrole.

TABLE B-27. KEY IONS AND RELATIVE ABUNDANCES FOR SAFROLE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	3.2	77	62.0	119	3.5	188	.2
42	.6	78	39.6	120	1.3	189	.3
45	.0	79	13.2	121	2.8		
		80	1.7	122	.8	211	.2
48	1.4	84	.1	123	.4		
49	2.4	86	.7	131	60.2	322	.2
50	19.5	87	1.6				
51	38.0	88	1.2	132	21.4		
52	11.0	89	4.4	133	5.0		
53	9.1			135	35.9		
54	1.0	91	10.8	136	3.0		
55	3.0	92	3.3	137	.4		
56	.4	93	.9	141	.1		
58	.6	94	.3	142	.3		
59	.1	95	.3	145	.4		
61	3.0	98	.6				
		103	59.0	147	1.3		
62	9.6			149	.2		
63	19.3	104	78.5	159	.8		
64	4.6	105	20.7				
65	10.2	106	3.7	161	33.1		
66	2.3	107	1.1	162	100.0		
67	1.2	108	.6	163	11.5		
68	.4	109	.2	164	1.6		
69	.2	115	2.8				
74	8.2	116	1.0	178	.2		
75	7.6	117	.6				

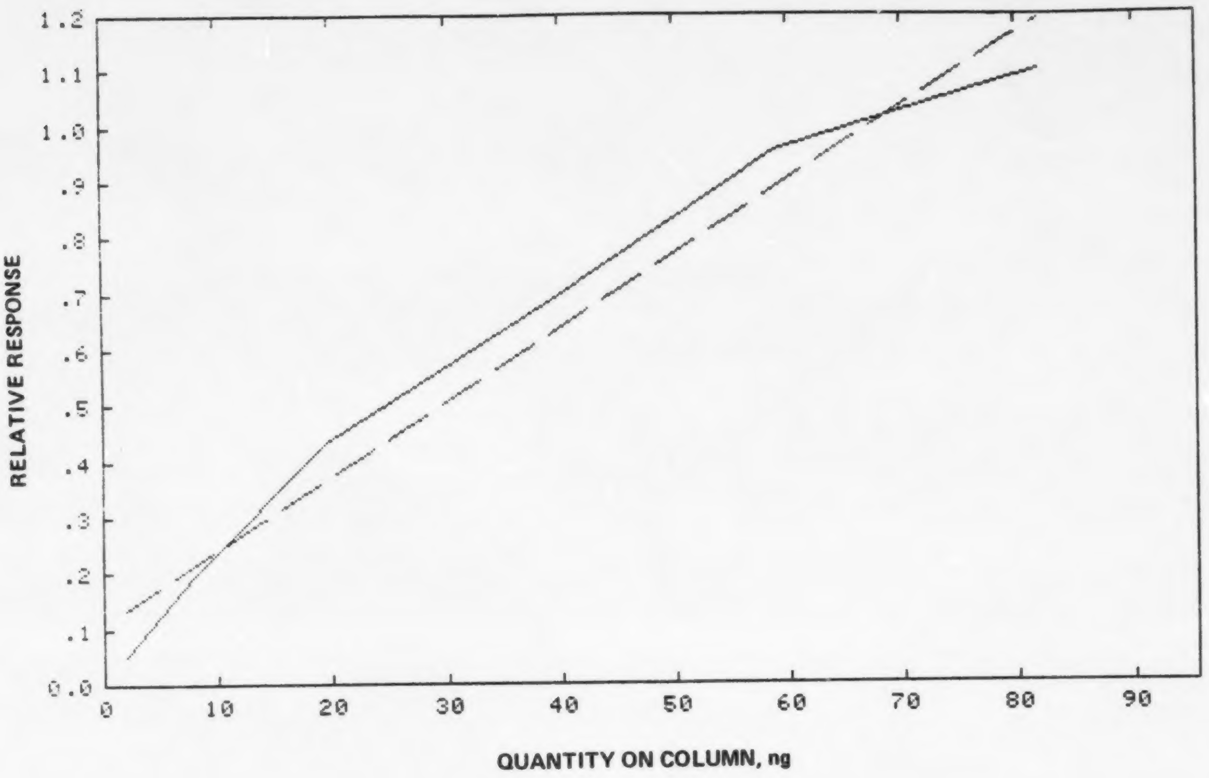
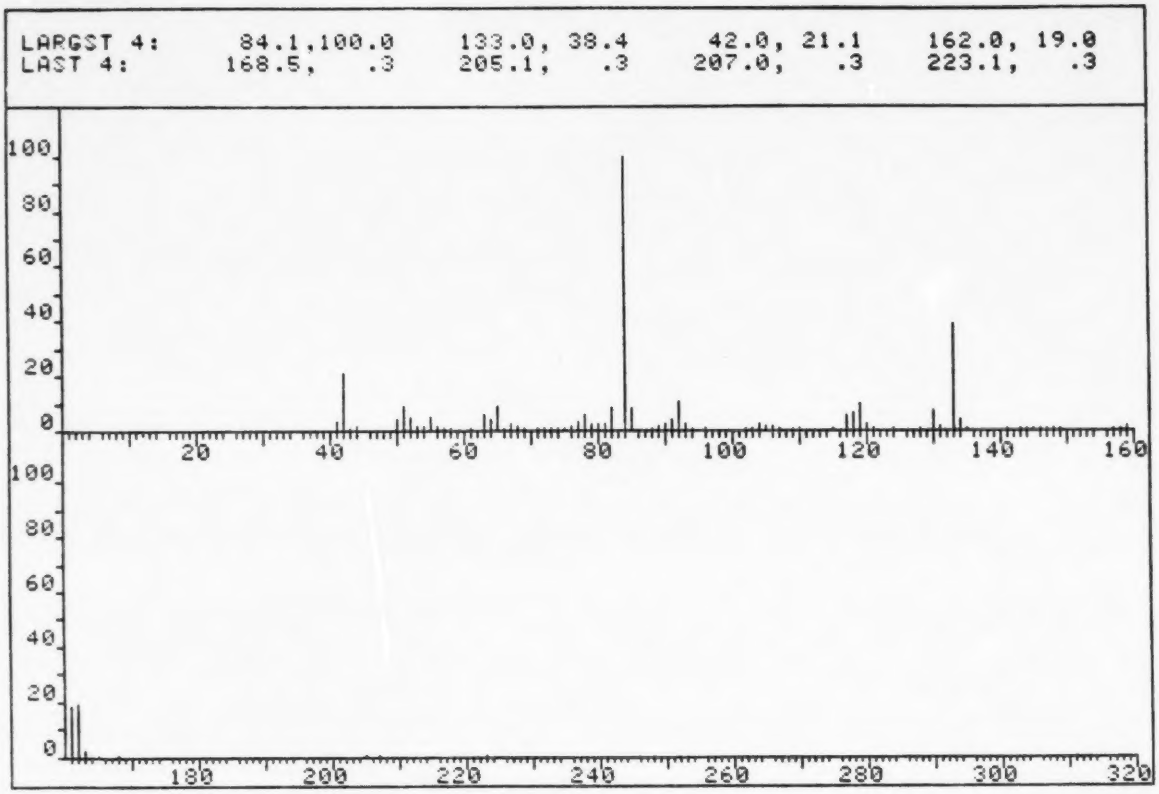


Figure B-60. Calibration curve for the determination of safrole by GC/MS.

Range: 7.8 - 82 ng
Correlation coefficient: 0.983
Slope: 1.3 x 10^{-2}
y-Intercept: 1.1 x 10^{-1}



```
LARGST 4:     84.1,100.0     133.0, 38.4     42.0, 21.1     162.0, 19.0
LAST 4:      168.5,    .3    205.1,    .3    207.0,    .3   223.1,    .3
```

Figure B-61. Mass spectrum for nicotine.

TABLE B-28. KEY IONS AND RELATIVE ABUNDANCES FOR NICOTINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	3.4	75	.8	109	.4	157	.4
42	21.1			110	.4	158	.4
43	.3	76	1.7	115	.3	159	1.5
44	2.0	77	2.9	117	5.4		
		78	5.9			161	18.2
50	4.2	79	2.2	118	6.2	162	19.0
51	9.1	80	2.2	119	9.6	163	1.7
52	5.1	81	2.6	120	2.2	165	.3
53	1.7	82	8.2	121	.3	168	.3
54	1.9	84	100.0	124	.3		
55	4.7	85	7.7	128	.5	205	.3
56	1.3	88	1.1	130	7.2	207	.3
57	.9	89	1.4	131	1.5		
58	.1					223	.3
61	.6	90	2.1	133	38.4		
		91	4.4	134	4.2		
63	5.7	92	10.7	135	.3		
64	4.0	93	2.3	141	.4		
65	8.7	94	.9	141	.1		
66	1.2	96	.4	143	.4		
67	2.6	102	.9	144	.9		
68	1.6	103	1.0	145	.6		
69	.6						
71	.8	104	2.6	146	.3		
72	.6	105	1.6	147	.7		
73	.3	106	1.8	148	.4		
74	1.1	107	1.1	149	.4		

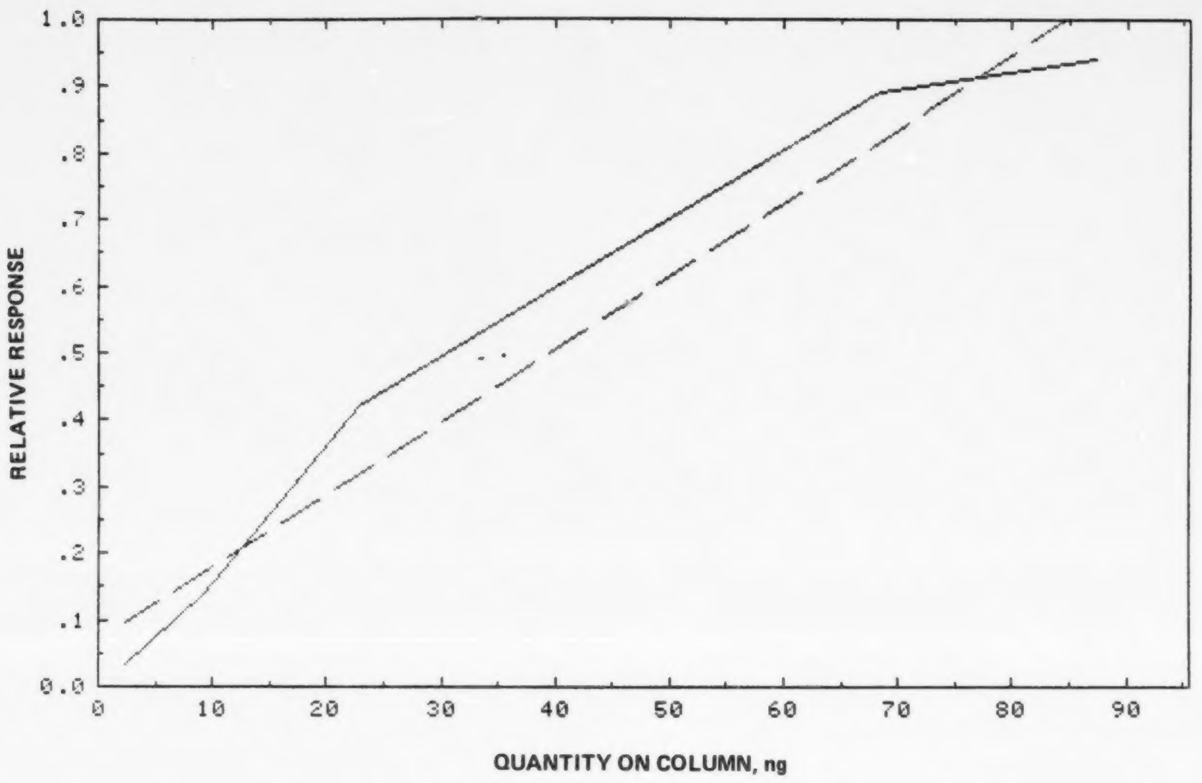
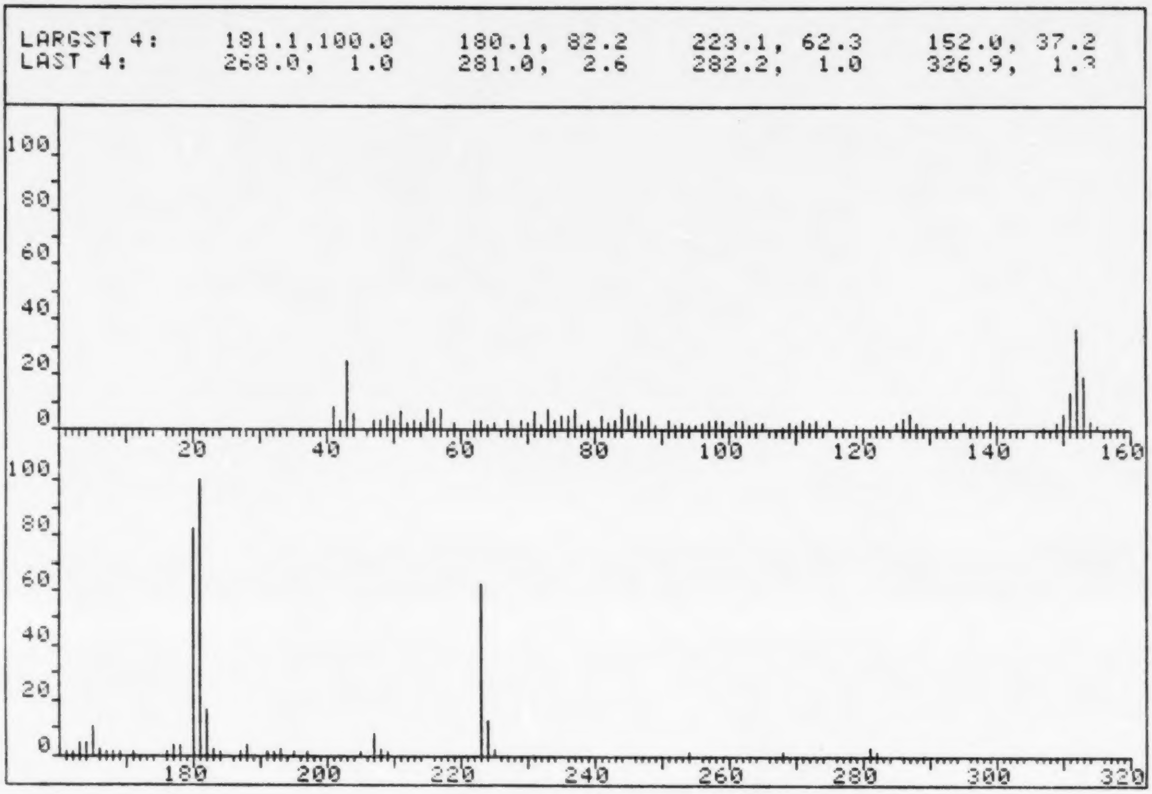


Figure B-62. Calibration curve for the determination of nicotine by GC/MS.

Range: 9.1 - 87 ng
Correlation coefficient: 0.980
Slope: 1.1 x 10^{-2}
y-Intercept: 7.2 x 10^{-2}



```
LARGST 4:     181.1,100.0     180.1, 82.2     223.1, 62.3     152.0, 37.2
LAST 4:       268.0,  1.0     281.0,  2.6     282.2,  1.0     326.9,  1.3
```

Figure B-63. Mass spectrum for 2-acetamidofluorene.

TABLE B-29. KEY IONS AND RELATIVE ABUNDANCES FOR 2-ACETAMIDOFLUORENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41	8.3	86	5.4	129	1.0	187	1.6
42	3.9	87	2.8	131	1.0	188	3.6
43	25.1	88	4.9	133	2.1	191	1.0
44	5.7	89	1.6	135	2.1	192	1.0
47	3.1	91	3.1	136	1.0	193	1.8
48	3.4	92	1.6	137	1.8	195	1.0
49	5.2	93	2.3	139	3.9	197	1.3
50	3.4	94	1.8	140	1.6	205	1.3
51	6.5	95	1.6	141	1.3	207	7.8
52	2.6	96	2.6	147	1.0	208	2.1
53	3.1	97	3.1	149	2.3	209	1.3
54	2.3	98	3.6	150	5.4	223	62.3
54	2.3	99	3.4	151	14.2	224	12.1
55	7.0	100	1.3	152	37.2	225	2.1
56	4.4	101	3.1	153	19.4	254	1.3
57	7.5	102	2.8	154	3.6	268	1.0
59	2.3	103	1.6	155	1.6	281	2.6
62	3.1	104	2.3	157	1.3	282	1.0
63	3.1	105	2.1	158	1.3	327	1.3
64	1.6	108	1.3	159	1.0		
65	2.6	109	2.3	161	1.3		
67	3.1	110	1.8	162	1.6		
69	3.6	111	3.4	163	4.4		
70	2.6	112	2.1	164	4.4		
71	6.7	113	2.8	165	10.3		
72	1.8	114	1.3	166	2.3		
73	7.0	115	3.1	167	1.6		
74	3.4	117	1.0	168	1.3		
75	5.2	119	1.6	169	1.3		
76	4.9	120	1.3	171	1.0		
77	7.0	122	1.8	176	1.3		
78	1.6	123	1.8	177	3.6		
79	3.6	125	2.6	178	3.6		
80	1.3	126	4.1	180	82.2		
81	4.7	127	5.4	181	100.0		
82	2.6	128	2.1	182	16.5		
83	3.1			183	2.1		
84	7.2			184	1.6		
85	4.9						

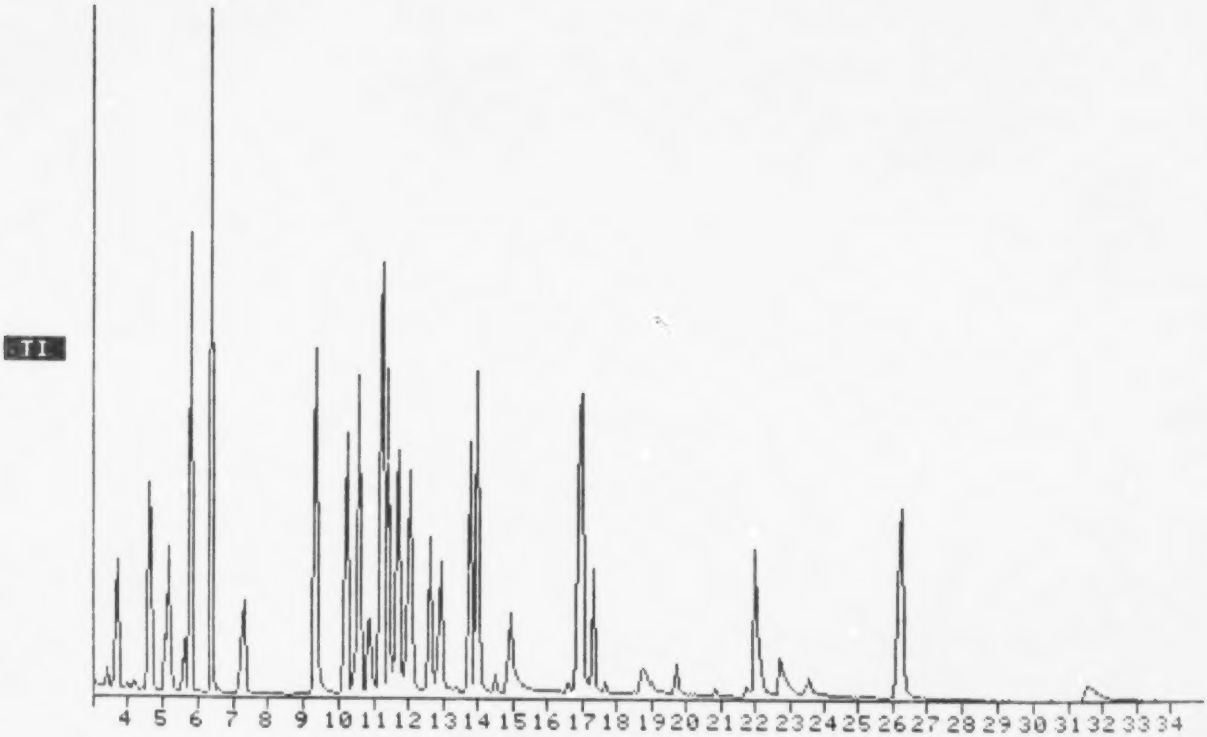


Figure B-64. Chromatogram by GC/MS for all candidate POHCs.

Temperature program:
40 °C, 0 min isothermal
40 °C to 280 °C at 10 °C/min
280 °C, 15 min isothermal

APPENDIX C

CHROMATOGRAMS, UV SPECTRA, AND CALIBRATION CURVES FOR HPLC/UV DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference UV Figure No.	Reference calibration curve Figure No.
3-(*alpha*-Acetonylbenzyl) -4-hydroxycoumarin	C-34	C-35	C-36
Acetophenetidine	C-17	C-18	C-19
Chlorambucil	C-48	C-49	C-50
4-Chloro-*m*-cresol	C-26	C-27	C-28, C-2
o-Chlorophenol	C-13	C-14	C-15, C-12
2,4-Dichlorophenol	C-30	C-31	C-32, C-3
2,4-Dichlorophenoxyacetic acid	C-51	C-52	C-53
4,6-Dinitro-*o*-cresol	C-60	C-61	C-62
Methyl yellow	C-60	C-63	C-64
4-Nitrophenol	C-9	C-10	C-11, C-1
N-Nitroso-*N*-methylurea	C-65	C-66	C-67
5-Nitro-*o*-toluidine	C-20	C-21	C-22
Phenol	C-5	C-6	C-7, C-8
Reserpine	C-45	C-46	C-47
Saccharin	C-68	C-69	C-70
Streptozotocin	C-1	C-2	C-3, C-4
2,3,4,6-Tetrachlorophenol	C-41	C-42	C-43, C-44
Tetramethylthiuram disulfide	C-23	C-24	C-25
2,4,6-Trichlorophenol	C-37	C-38	C-39, C-40
2,4,5-Trichlorophenoxyacetic acid	C-54	C-55	C-56

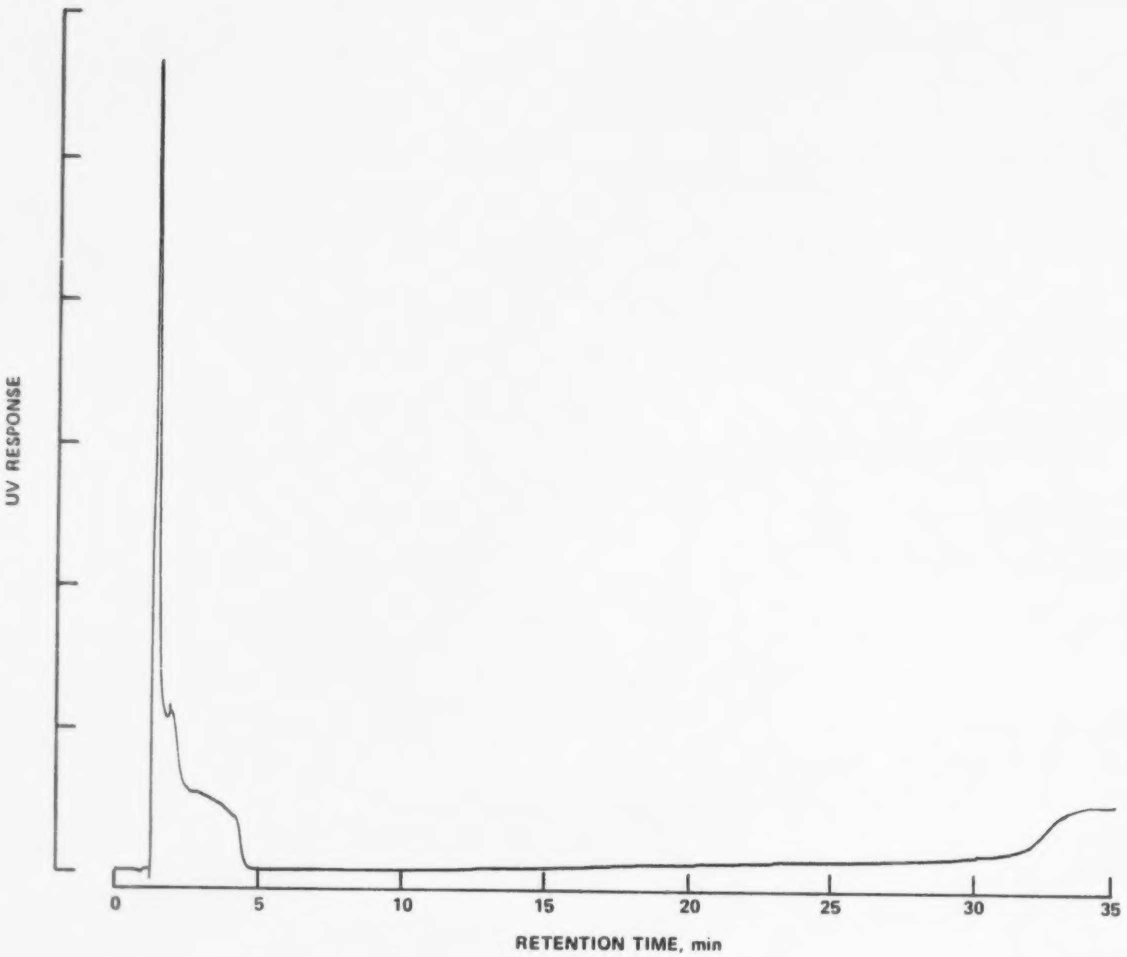


Figure C-1. Chromatogram by HPLC/UV for streptozotocin.

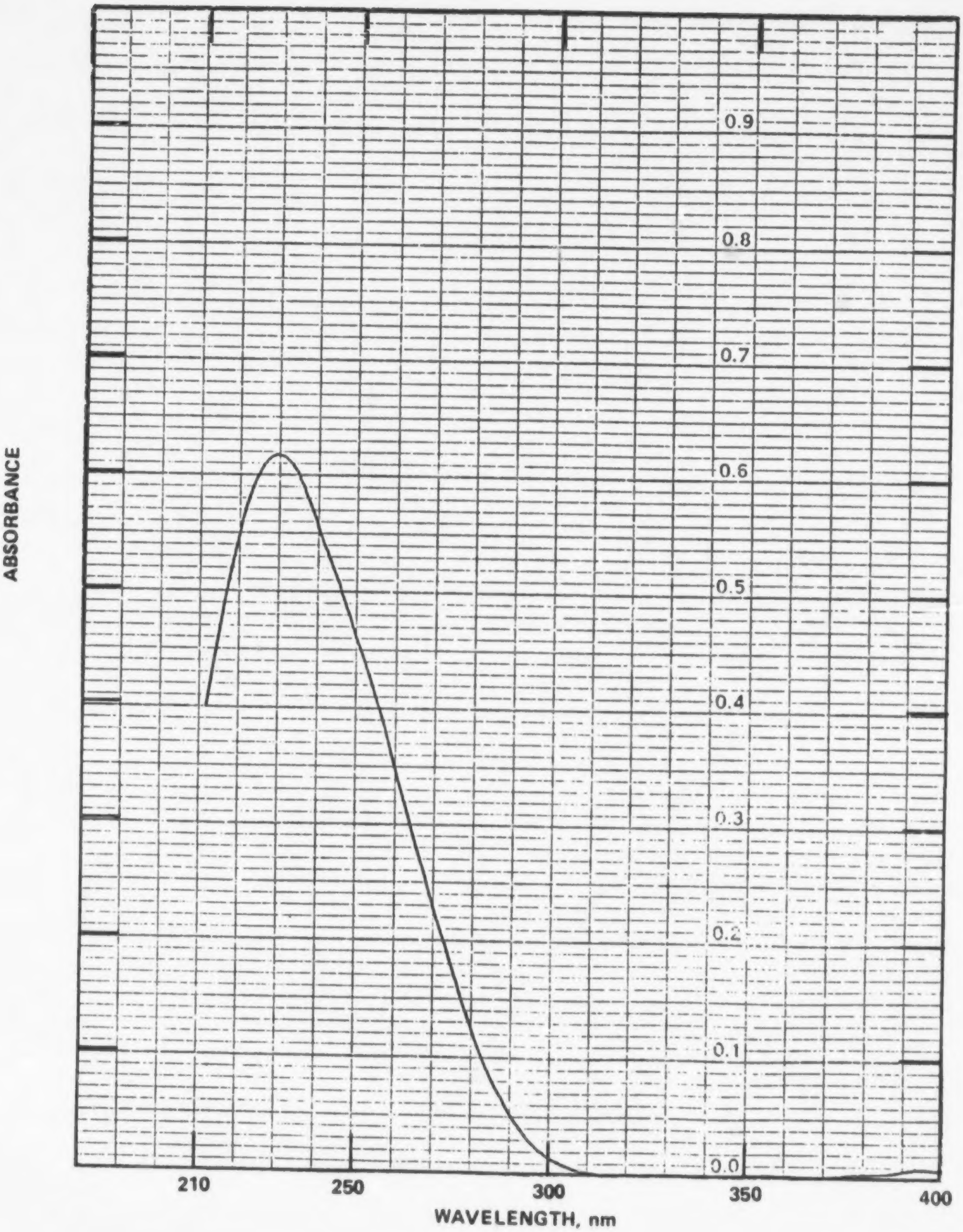


Figure C-2. UV spectrum of streptozotocin.

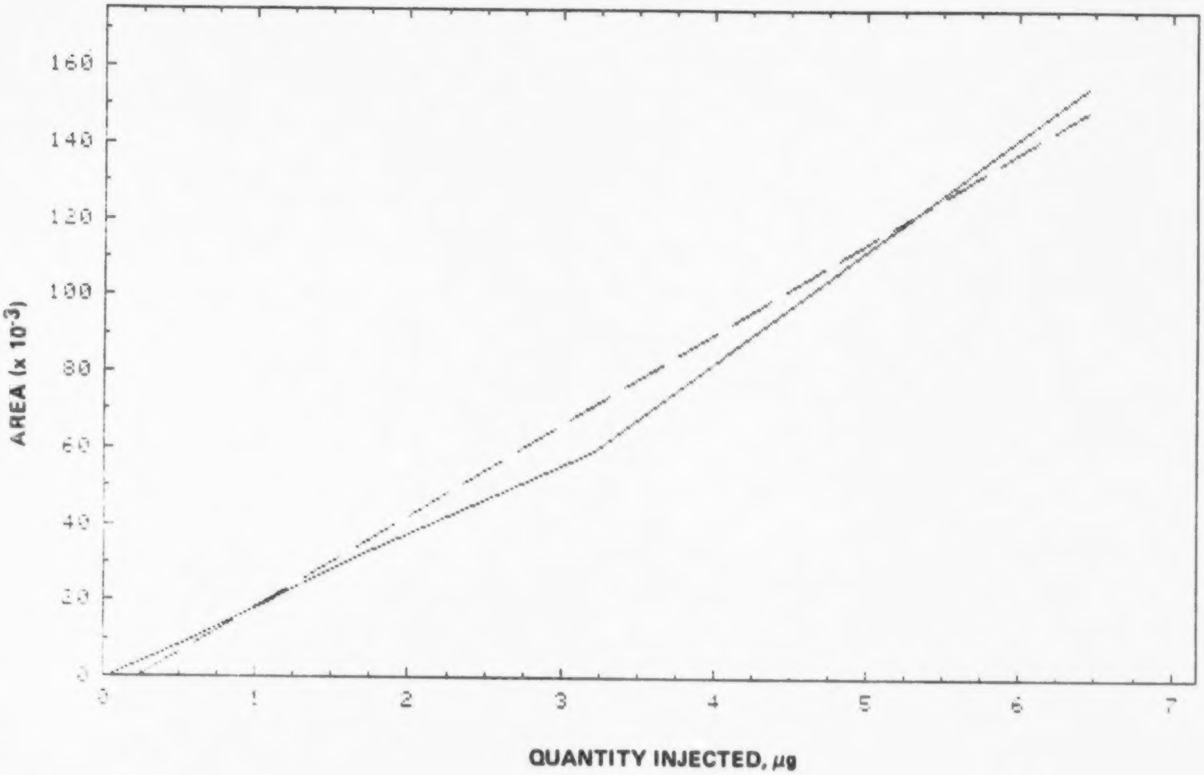


Figure C-3. Calibration curve for the determination of streptozotocin by HPLC/UV.

Range: 0.064 - 6.4 ug
Correlation coefficient: 0.993
Slope: $2.4 \times 10^{+1}$
y-Intercept: -5.4

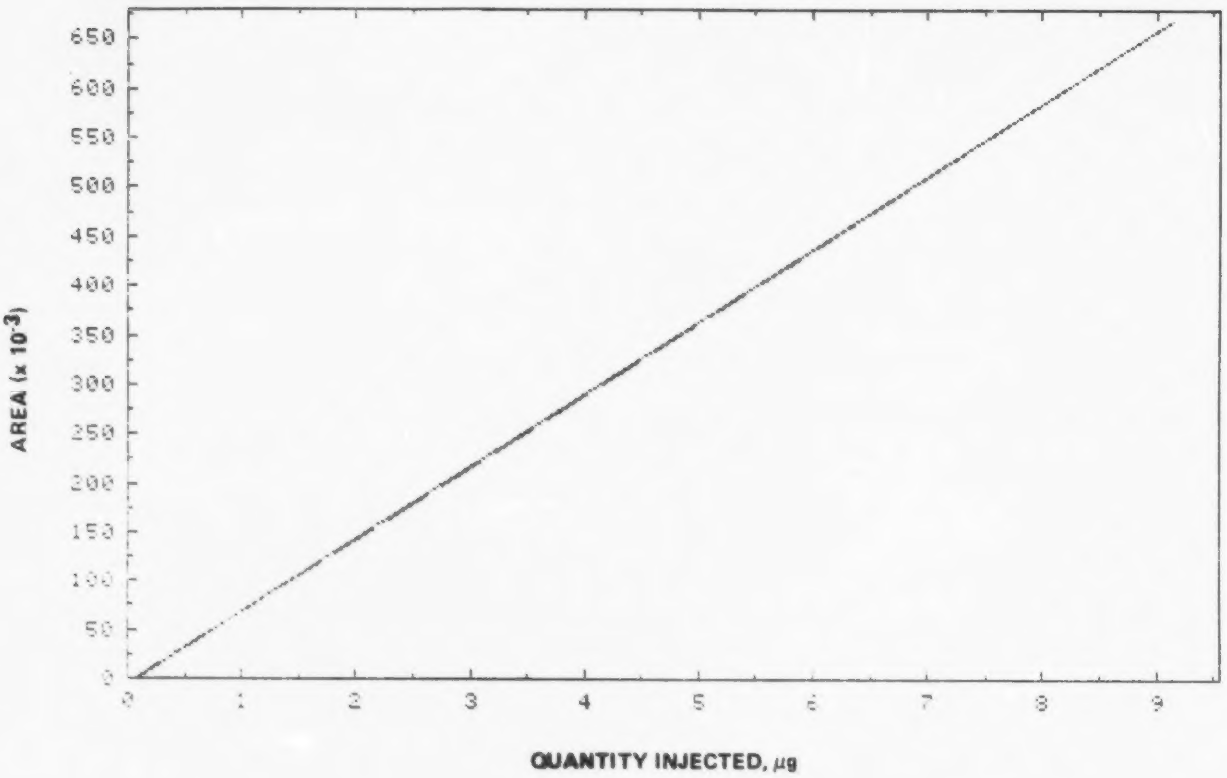


Figure C-4. Calibration curve for the determination of streptozotocin by HPLC/UV(280nm).

Range: 0.64 - 9.2 μg
Correlation coefficient: 0.999
Slope: $7.4 \times 10^{+1}$
y-Intercept: -4.9

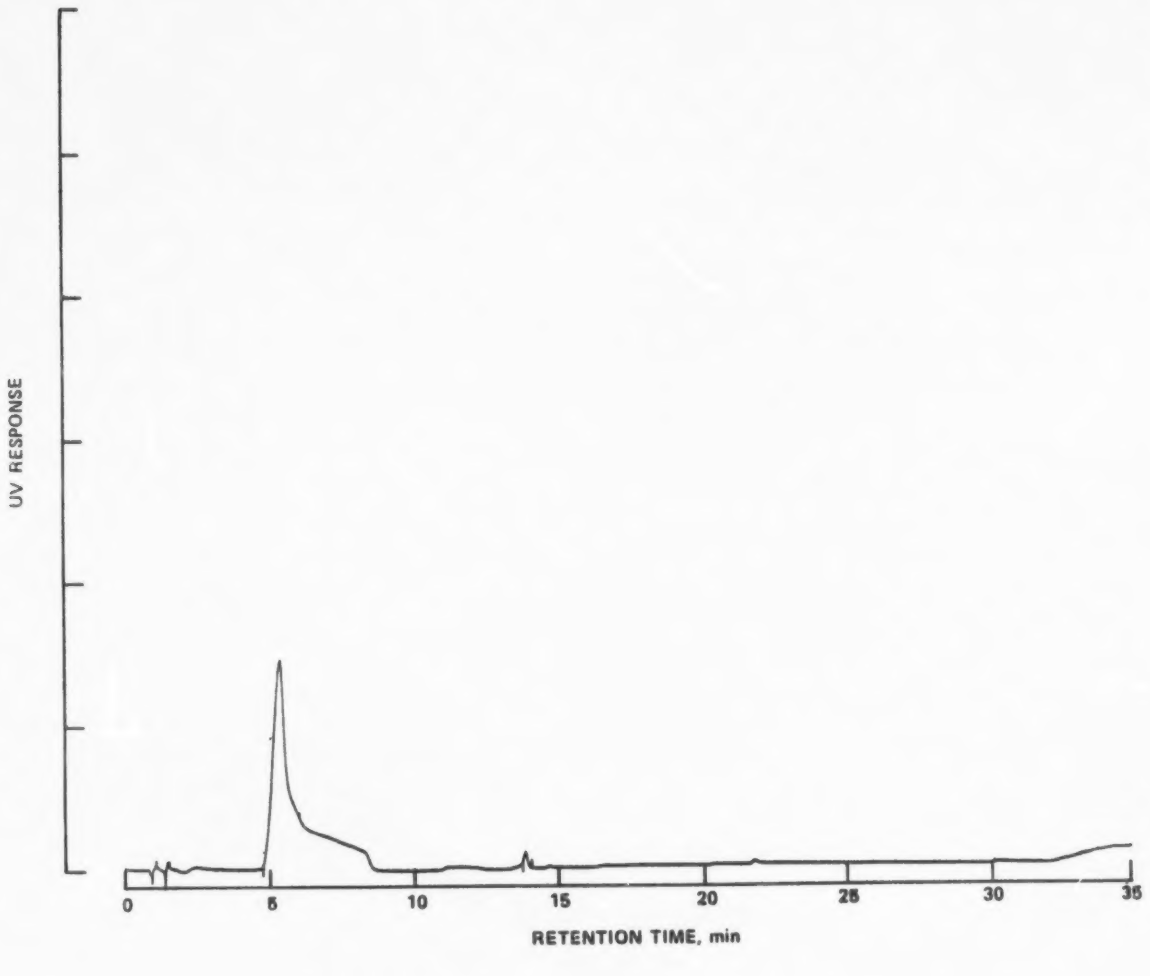


Figure C-5. Chromatogram by HPLC/UV for phenol.

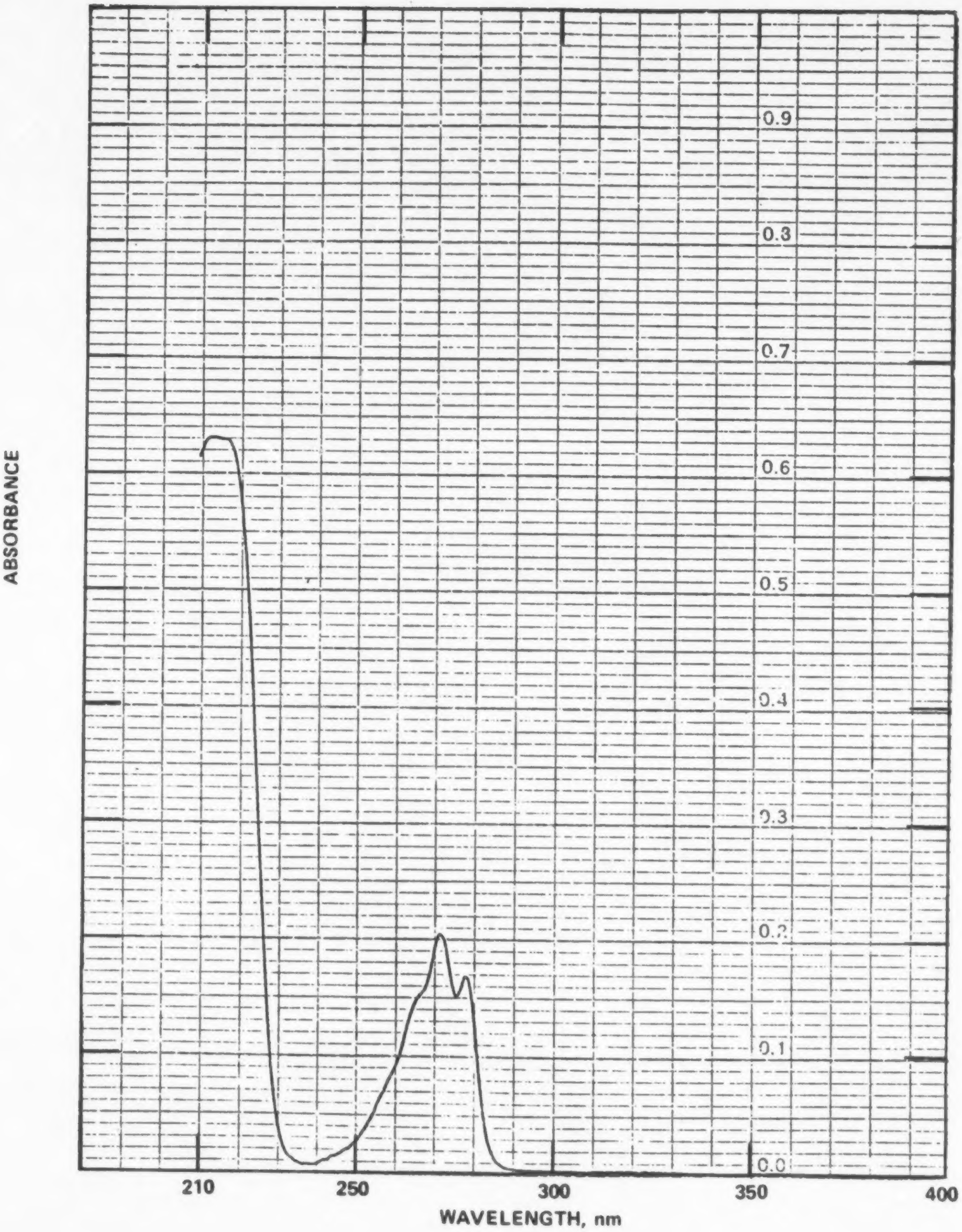


Figure C-6. UV spectrum of phenol.

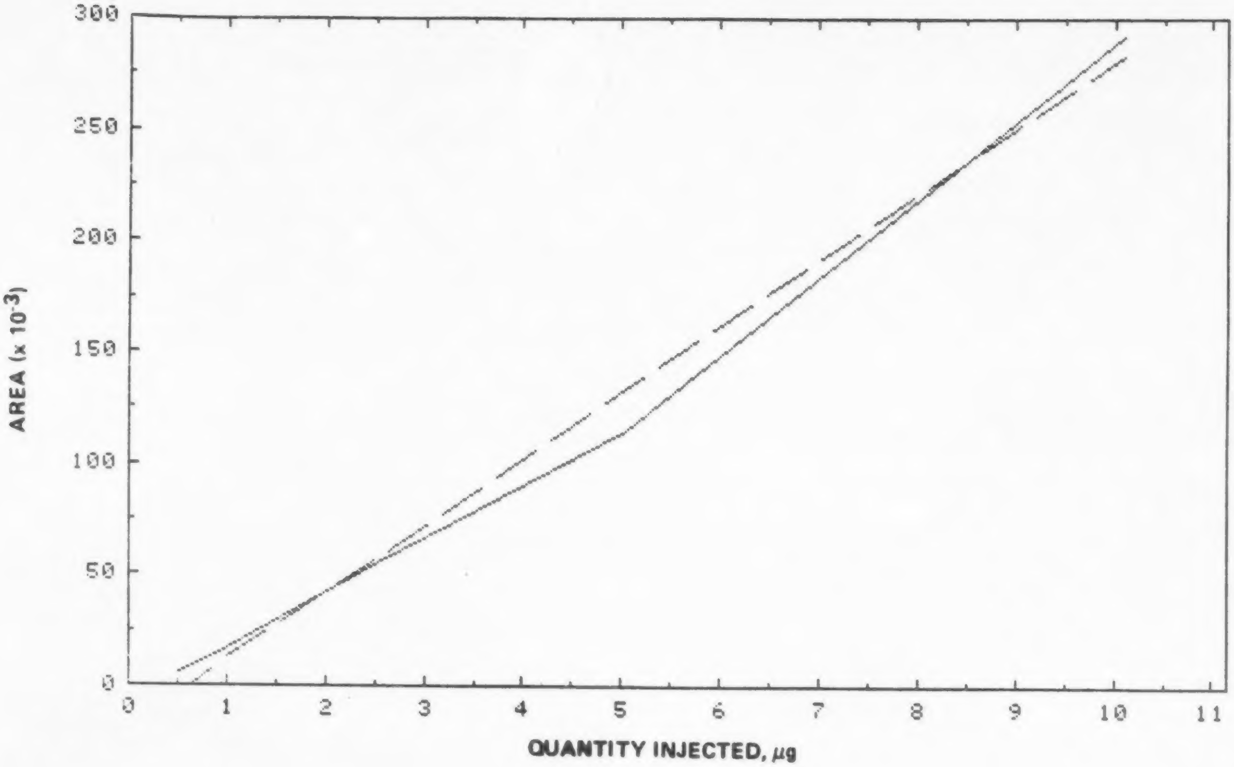


Figure C-7. Calibration curve for the determination of phenol by HPLC/UV.

Range: 2.5 - 10 μg
Correlation coefficient: 0.995
Slope: $3.0 \times 10^{+1}$
y-Intercept: $-1.7 \times 10^{+1}$

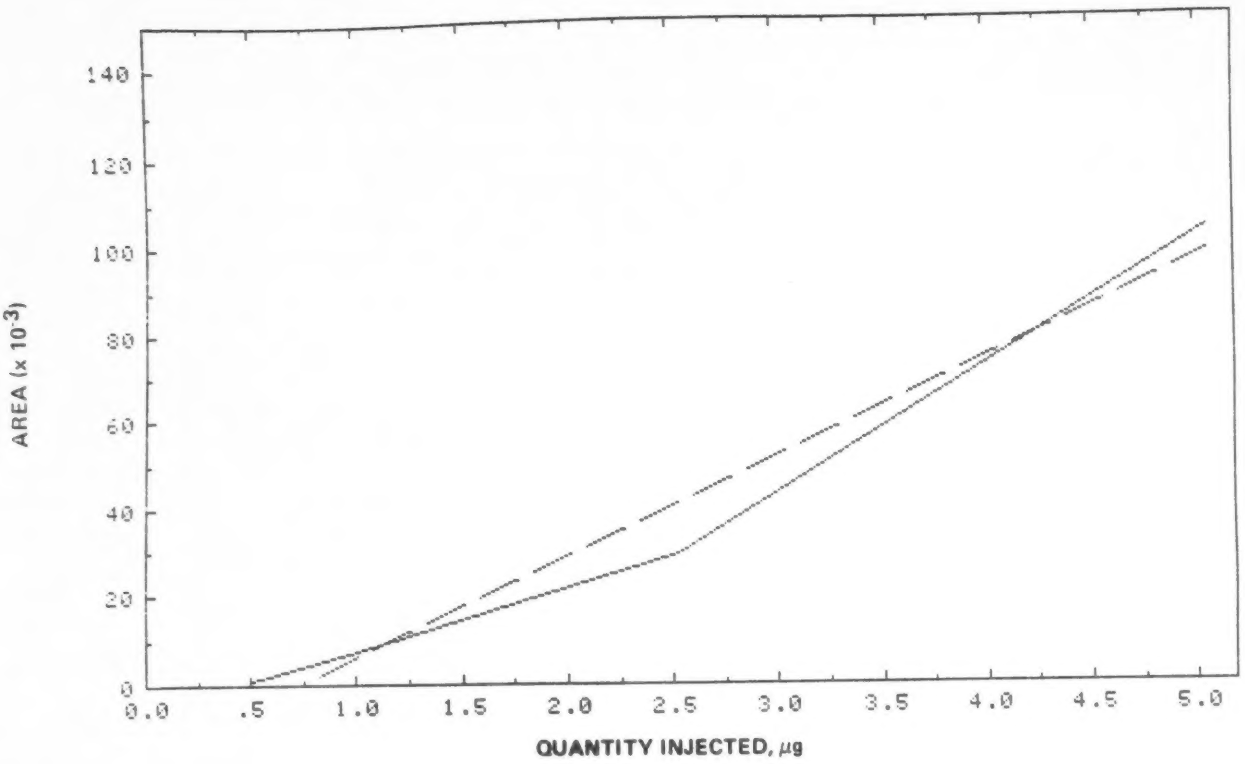


Figure C-8. Calibration curve for the determination of phenol by HPLC/UV(280nm).

Range: 1.0 - 5.0 µg
Correlation coefficient: 0.985
Slope: $2.2 \times 10^{+1}$
y-Intercept: $-1.6 \times 10^{+1}$

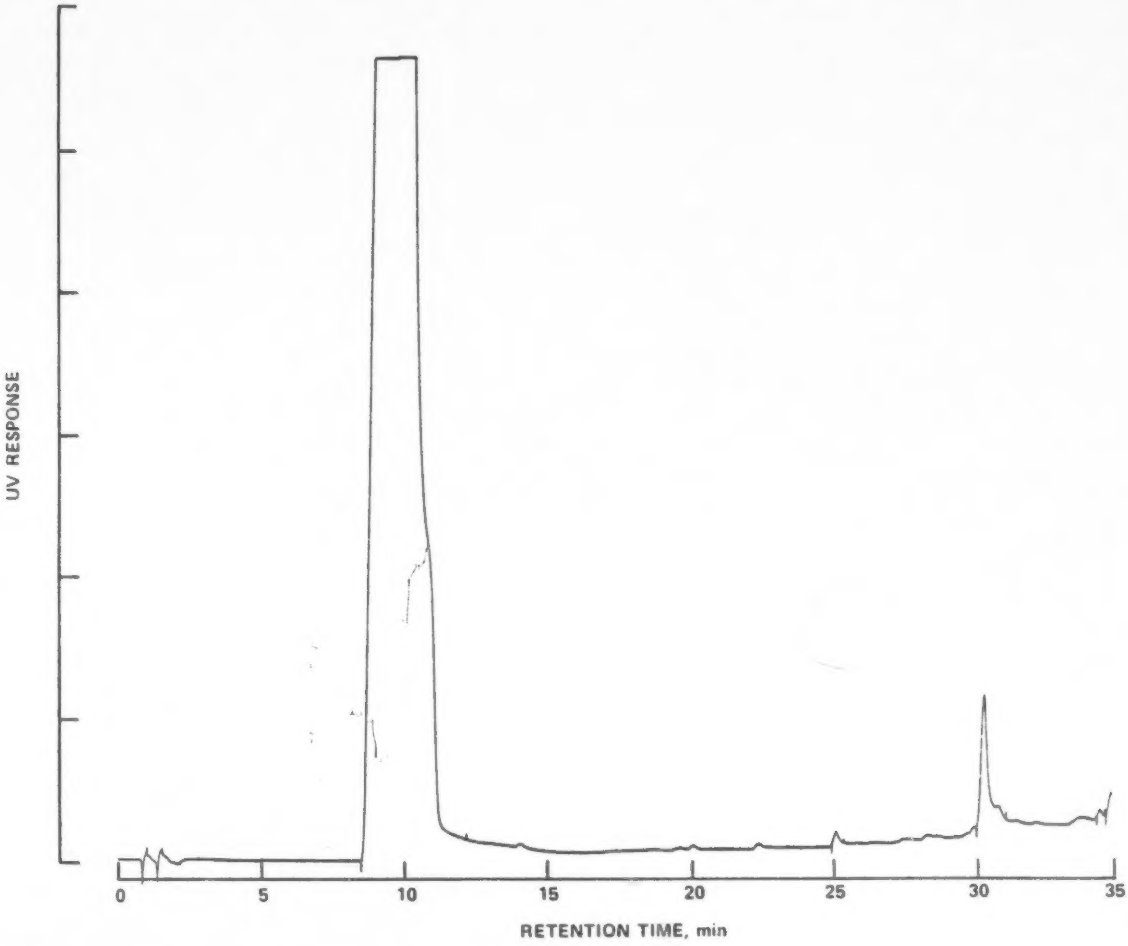


Figure C-9. Chromatogram by HPLC/UV for 4-nitrophenol.

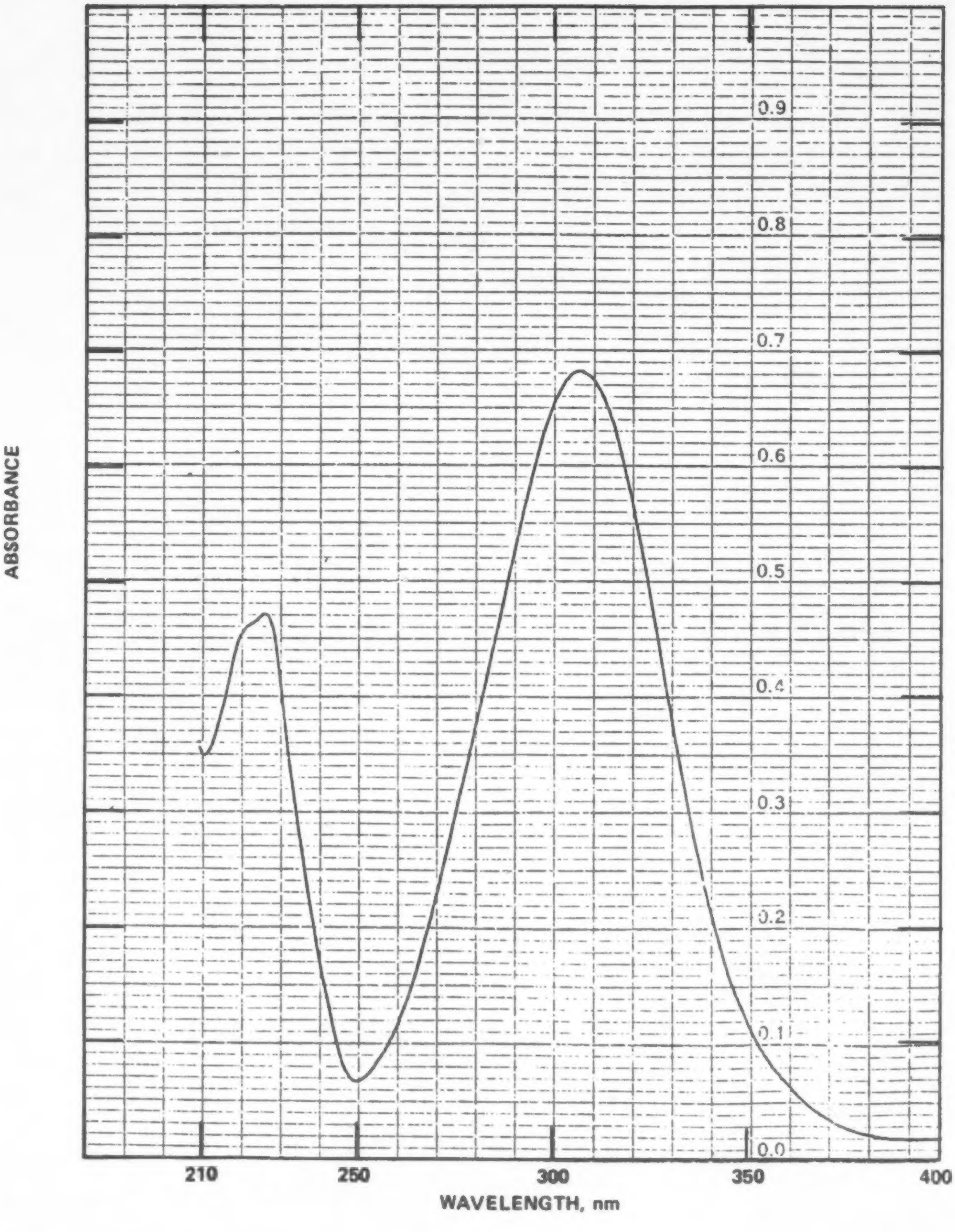


Figure C-10. UV spectrum of 4-nitrophenol.

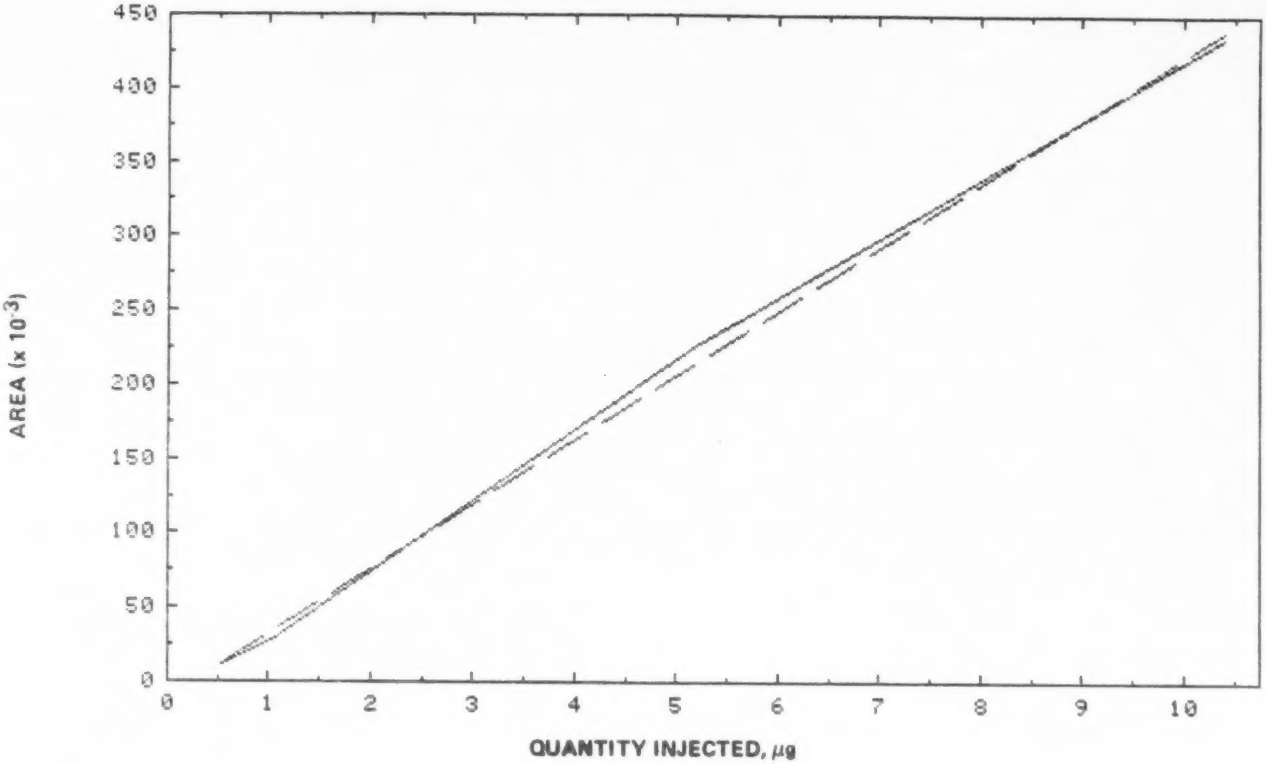


Figure C-11. Calibration curve for the determination of 4-nitrophenol by HPLC/UV.

Range: 0.52 - 10 µg
Correlation coefficient: 0.999
Slope: $4.3 \times 10^{+1}$
y-Intercept: $-1.1 \times 10^{+1}$

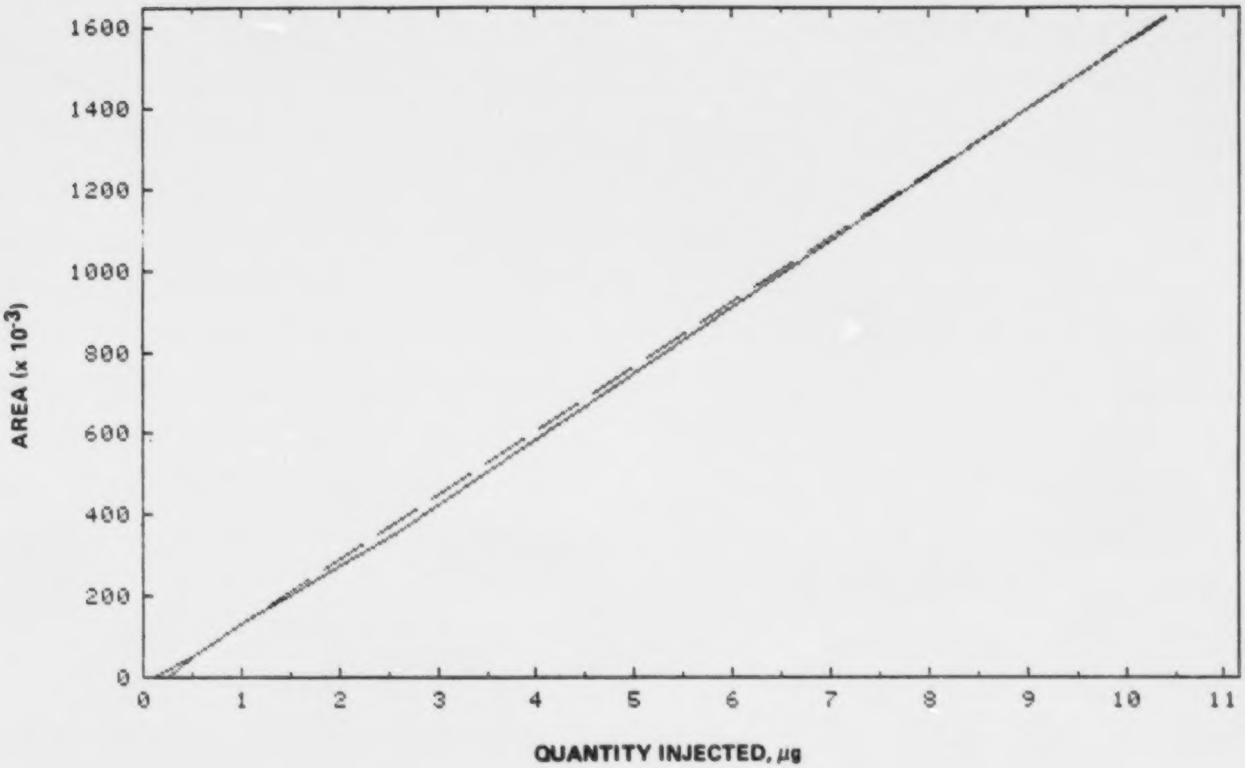


Figure C-12. Calibration curve for the determination of 4-nitrophenol by HPLC/UV(280nm).

Range: 0.52 - 10 μg
Correlation coefficient: 0.999
Slope: $1.6 \times 10^{+2}$
y-Intercept: $-2.9 \times 10^{+1}$

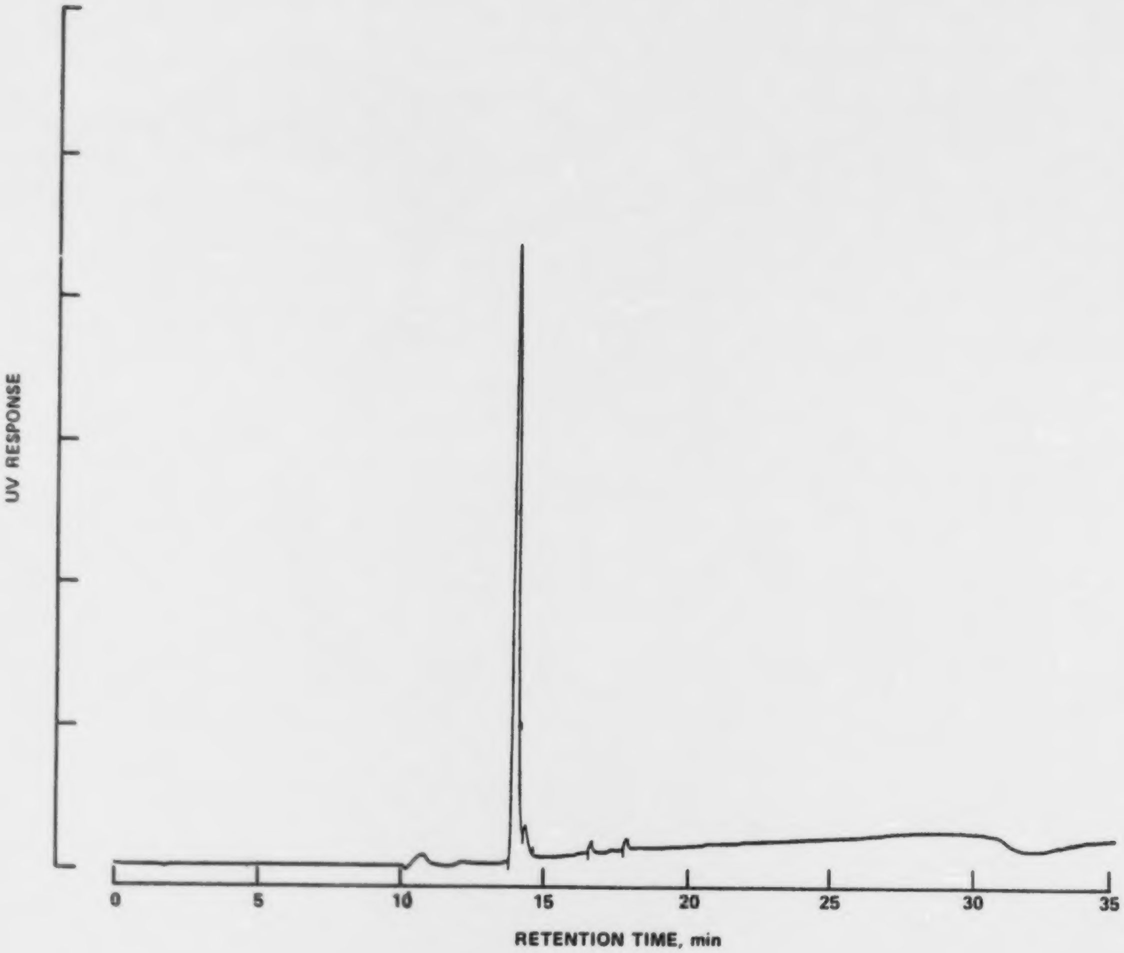


Figure C-13. Chromatogram by HPLC/UV for
o-chlorophenol.

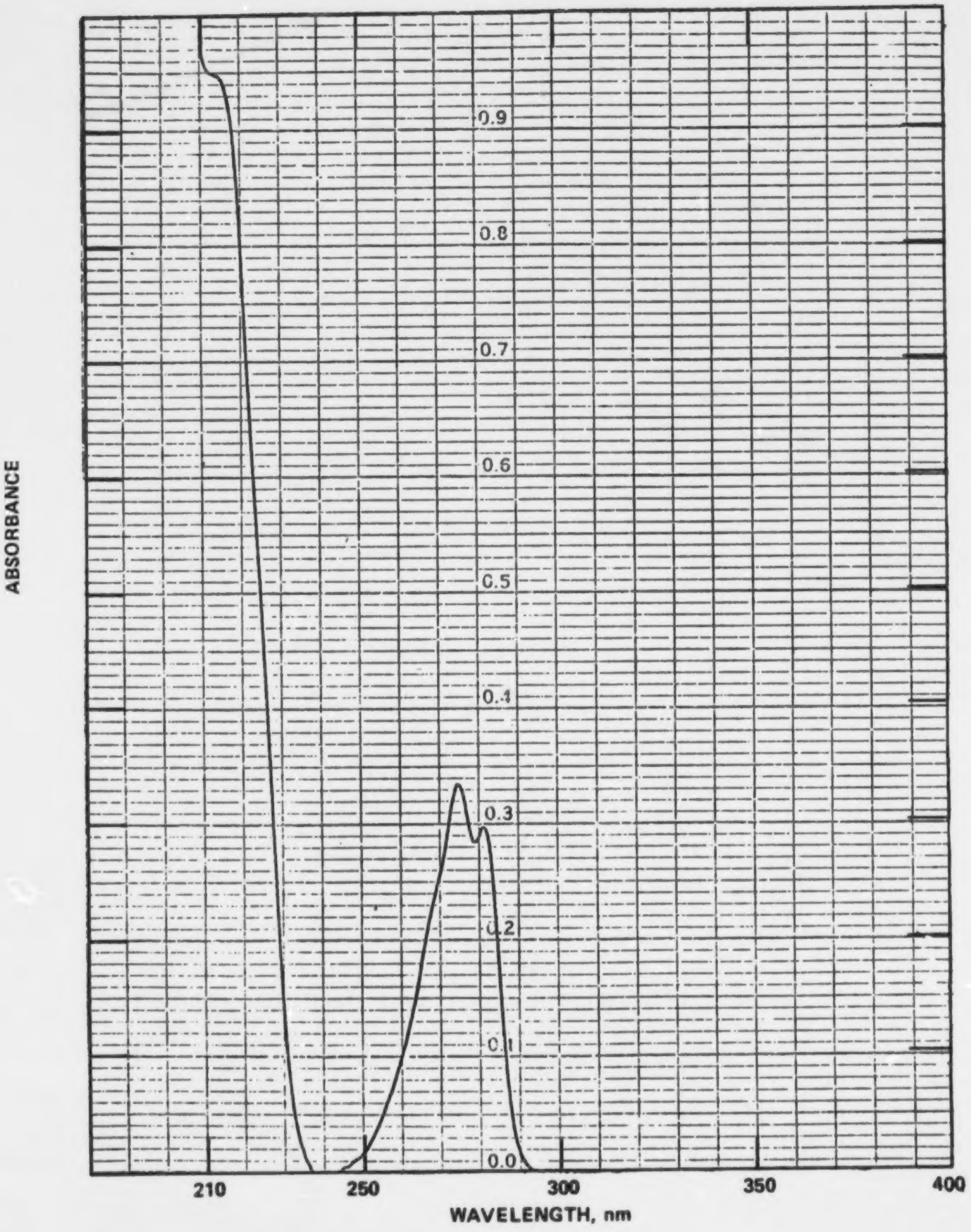


Figure C-14. UV spectrum of o-chlorophenol.

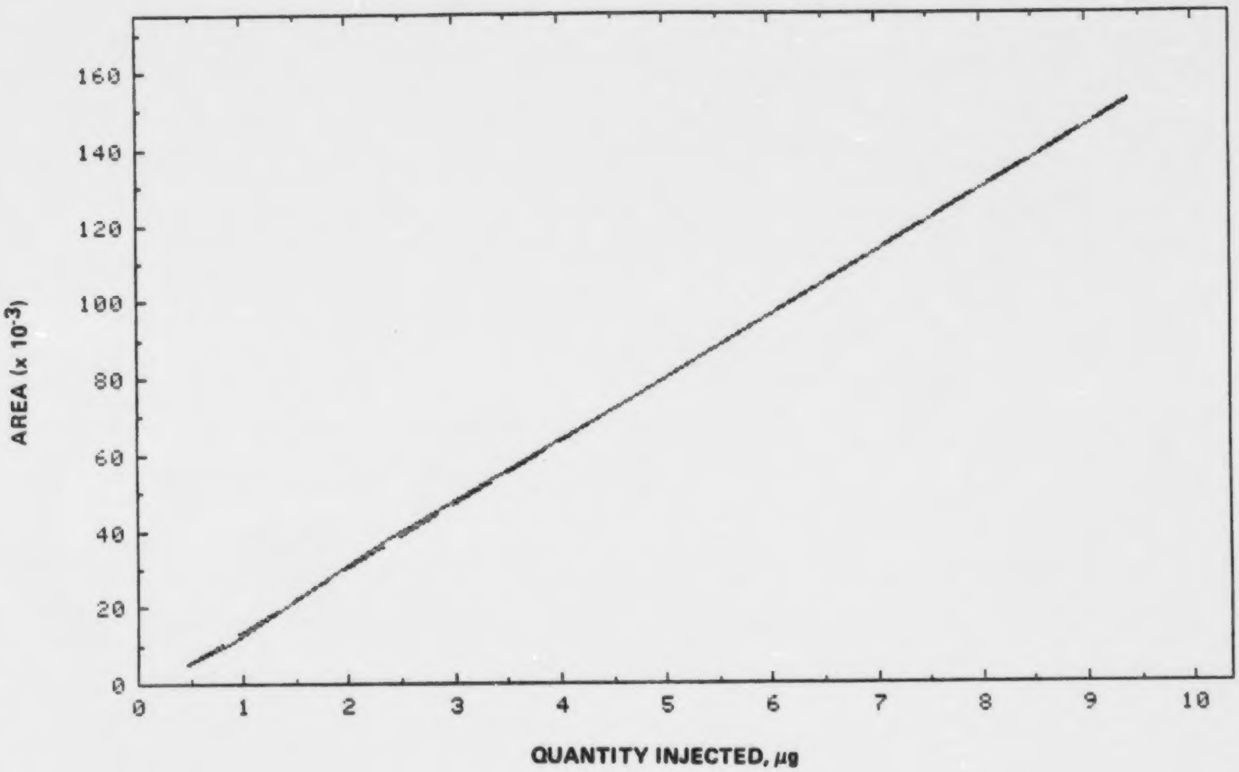


Figure C-15. Calibration curve for the determination of o-chlorophenol by HPLC/UV.

Range: 0.47 - 9.4 μg
Correlation coefficient: 0.999
Slope: 1.6 x 10^{+1}
y-Intercept: -2.6

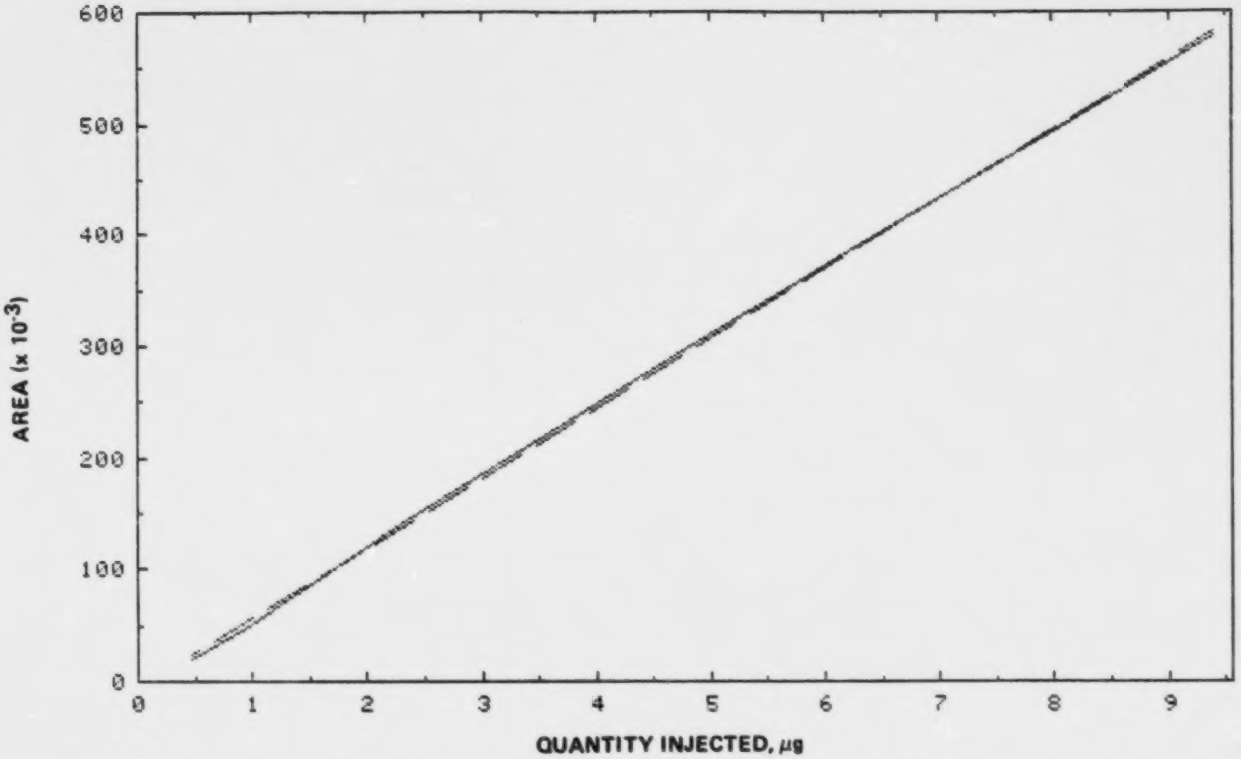


Figure C-16. Calibration curve for the determination of o-chlorophenol by HPLC/UV(280nm).

Range: 0.47 - 9.4 µg
Correlation coefficient: 0.999
Slope: $6.3 \times 10^{+1}$
y-Intercept: -6.5

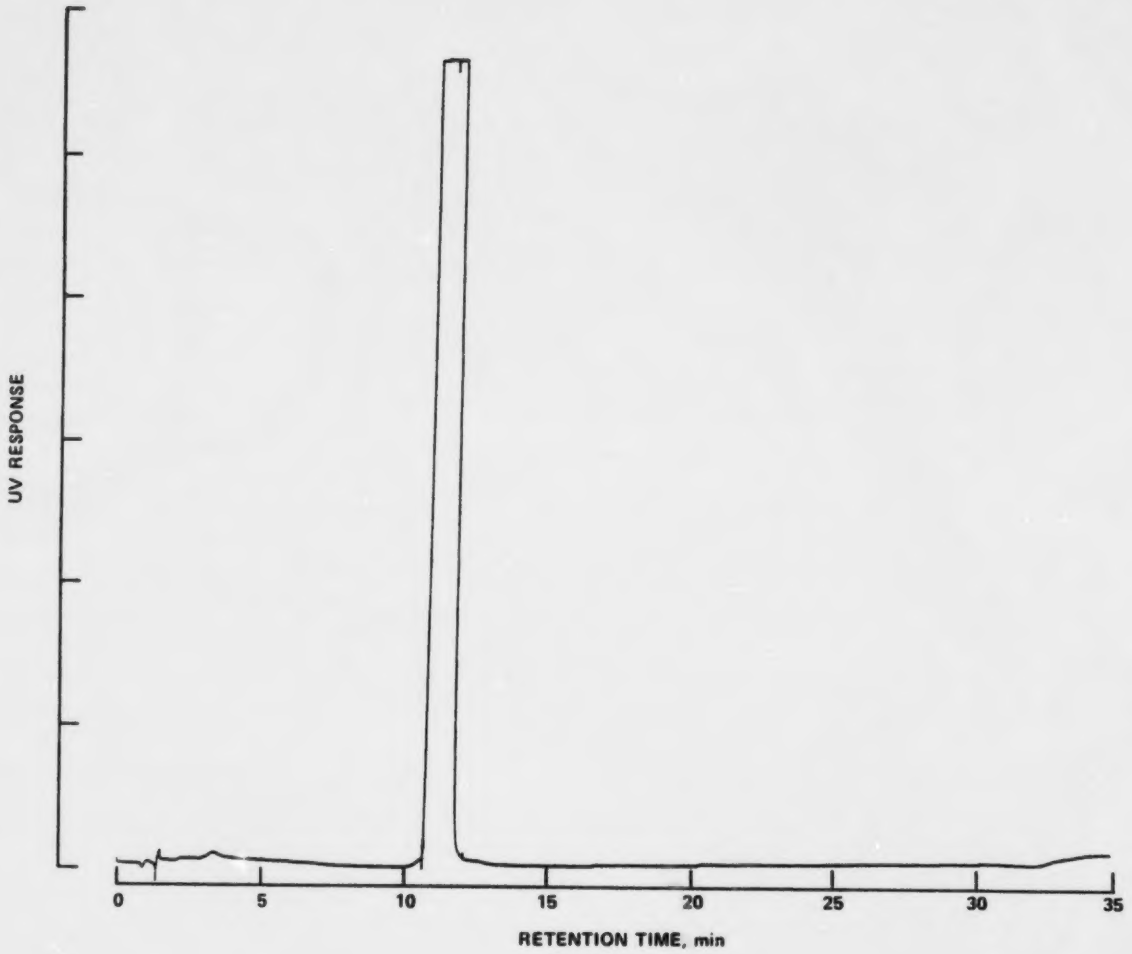


Figure C-17. Chromatogram by HPLC/UV for acetophenetidine.

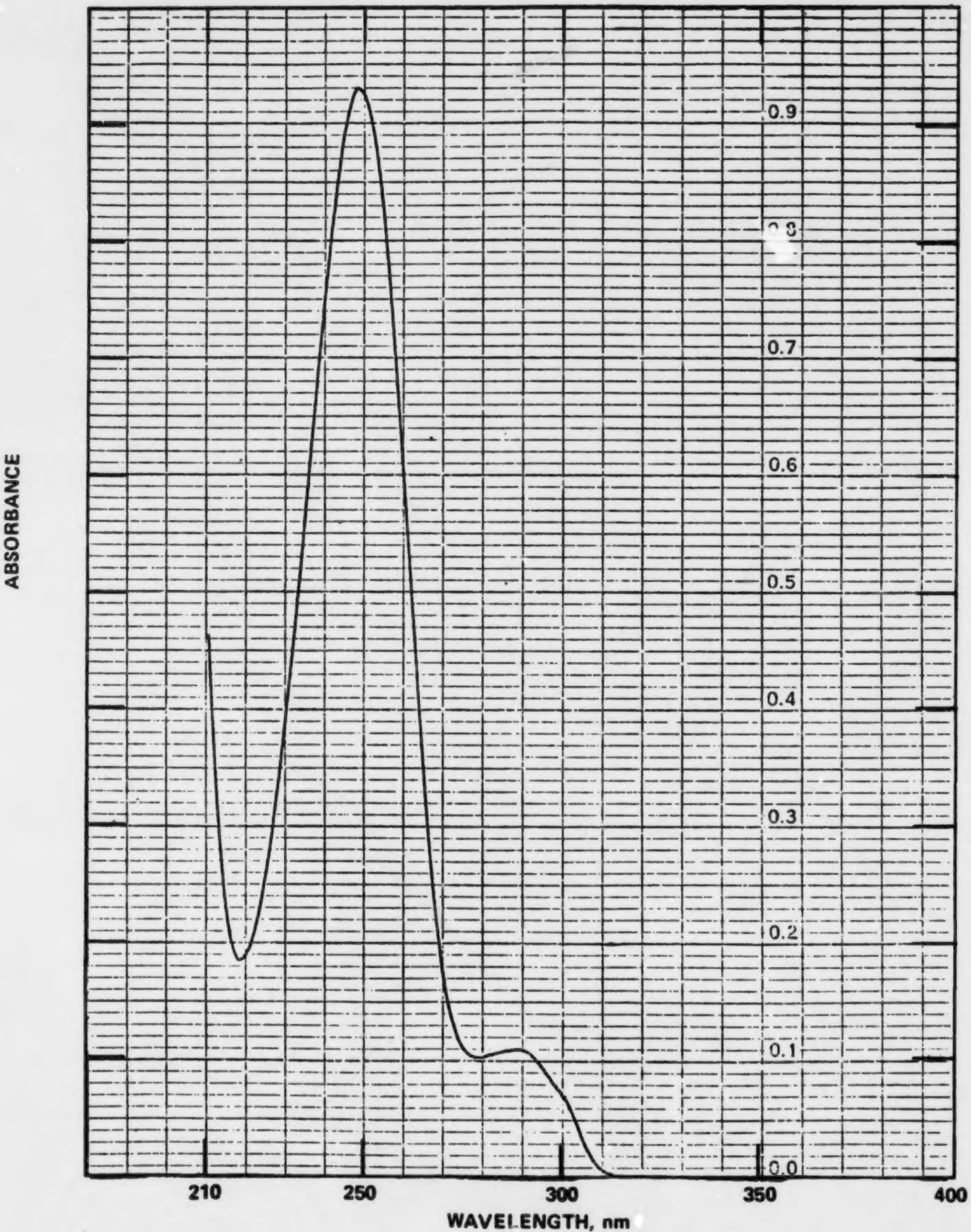


Figure C-18. UV spectrum of acetophenetidine.

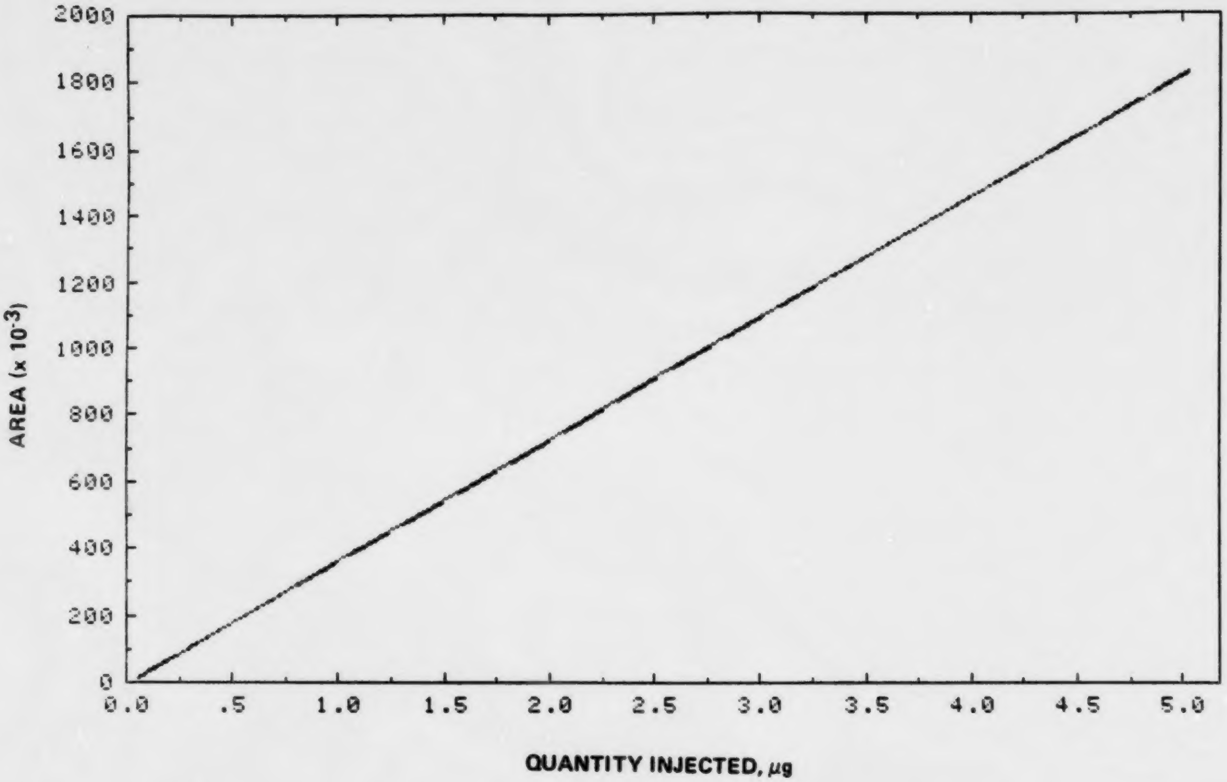


Figure C-19. Calibration curve for the determination of acetophenetidine by HPLC/UV.

Range: 0.050 - 5.0 µg
Correlation coefficient: 0.999
Slope: $3.6 \times 10^{+2}$
y-Intercept: -5.3

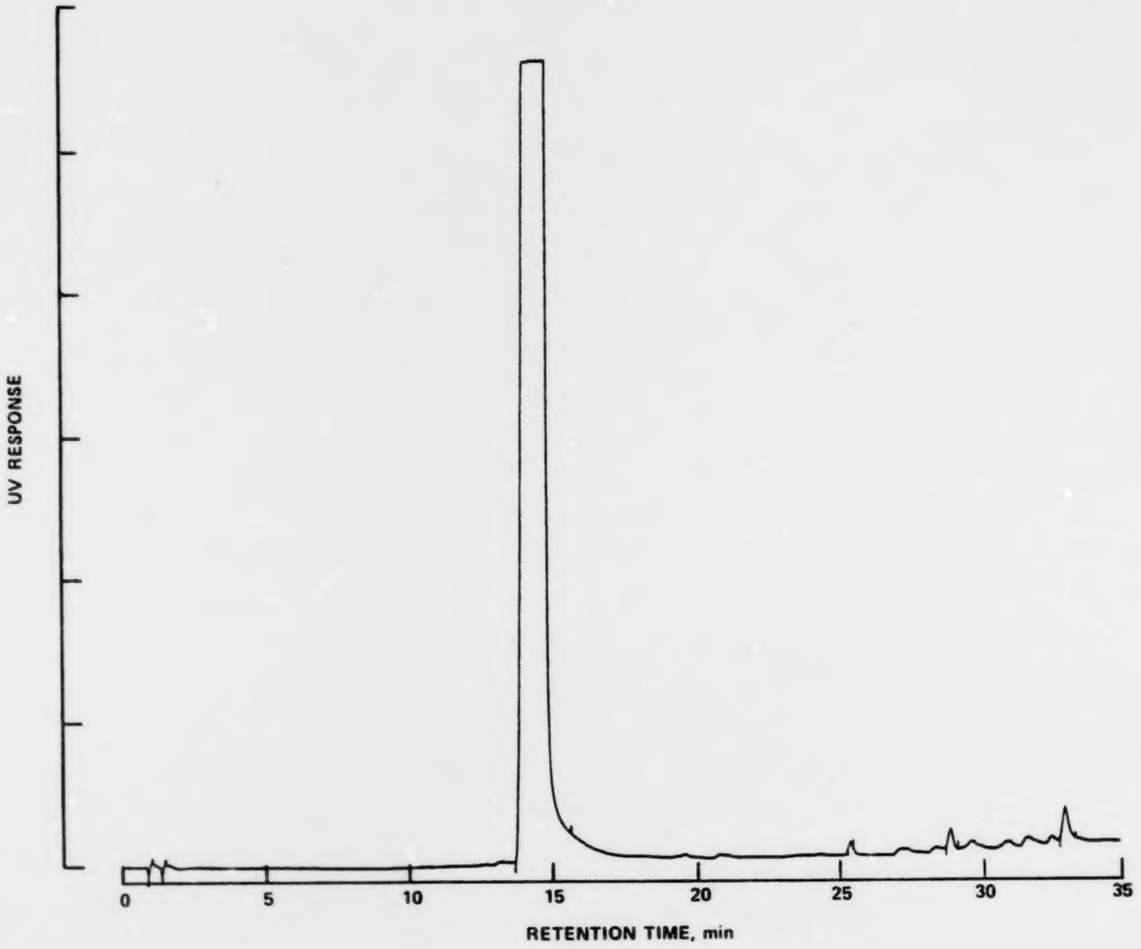


Figure C-20. Chromatogram by HPLC/UV for 5-nitro-o-toluidine.

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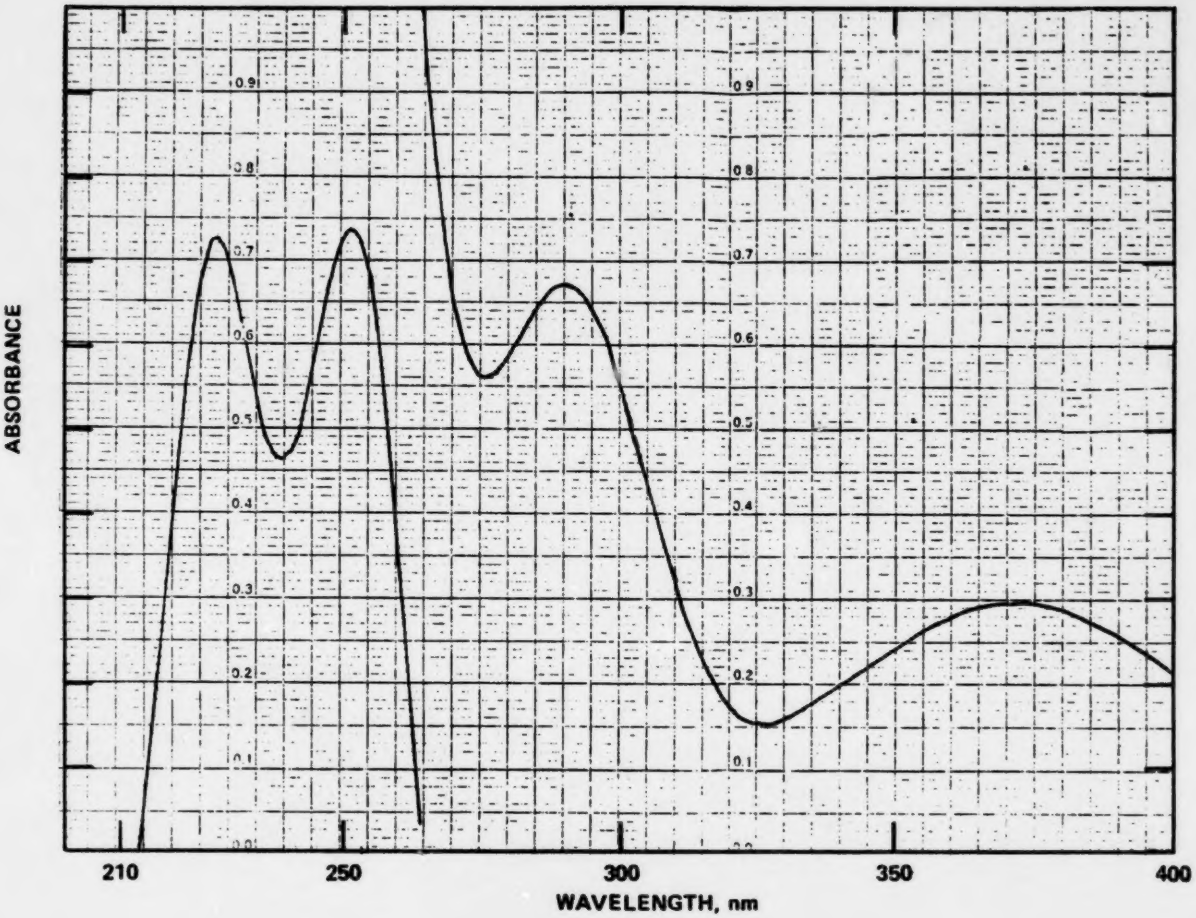

Figure C-21. UV spectrum of 5-nitro-o-toluidine.

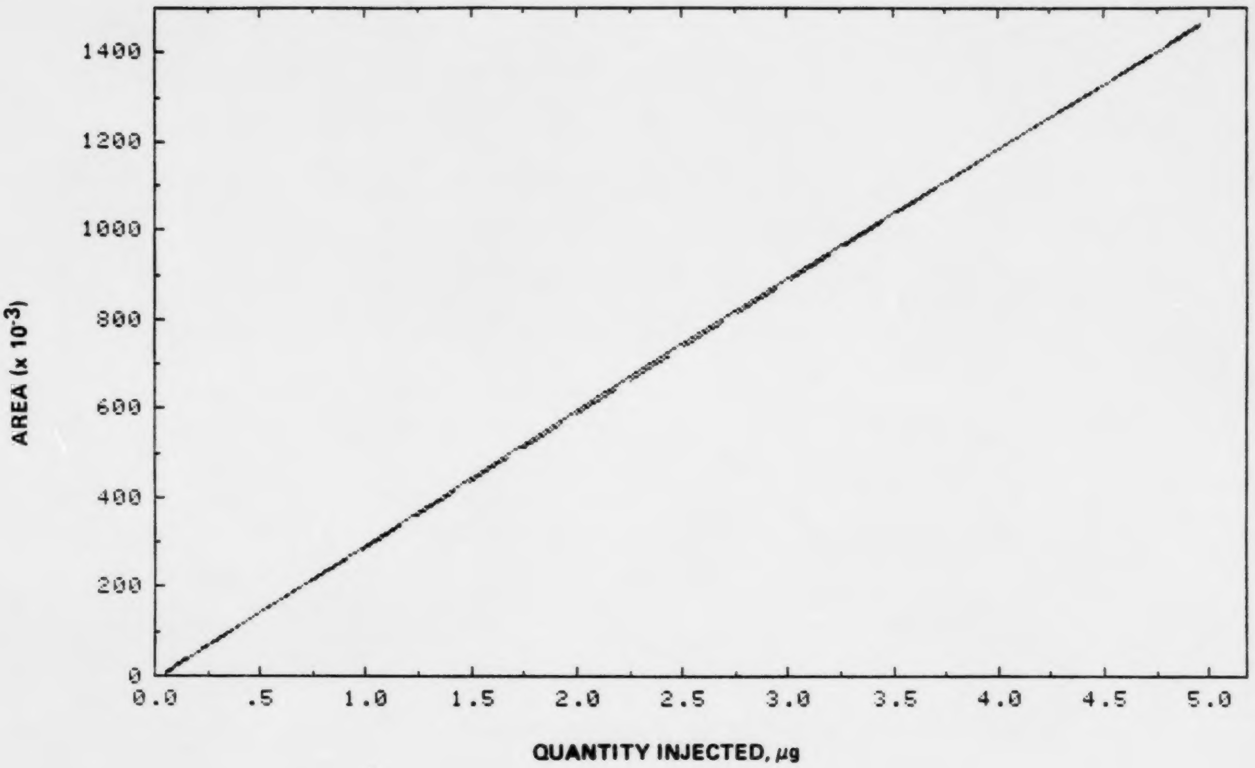

Figure C-22. Calibration curve for the determination of 5-nitro-o-toluidine by HPLC/UV

Range: 0.050 - 5.0 µg
Correlation coefficient: 0.999
Slope: $3.0 \times 10^{+2}$
y-Intercept: -6.0

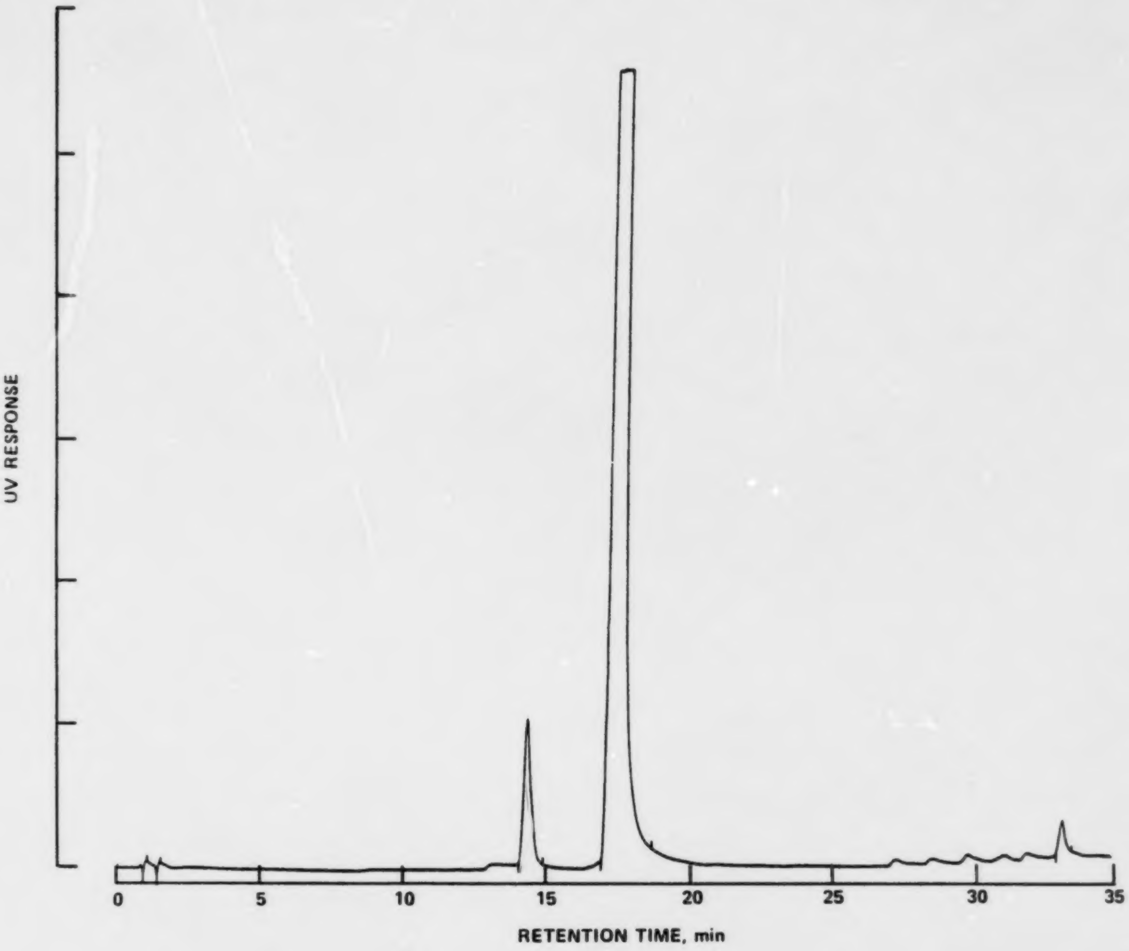

Figure C-23. Chromatogram by HPLC/UV for tetramethylthiuram disulfide.

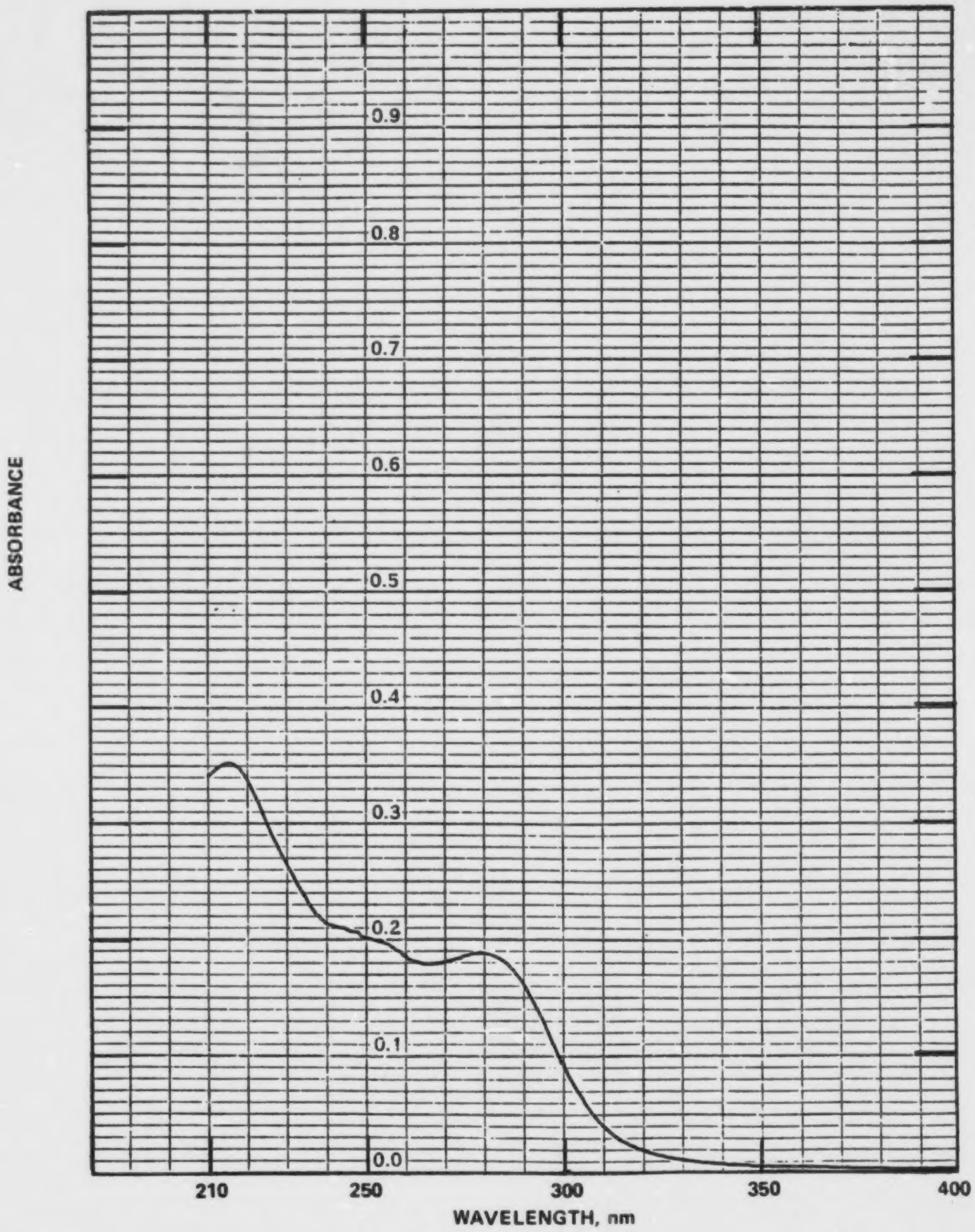

Figure C-24. UV spectrum of tetramethylthiuram disulfide.

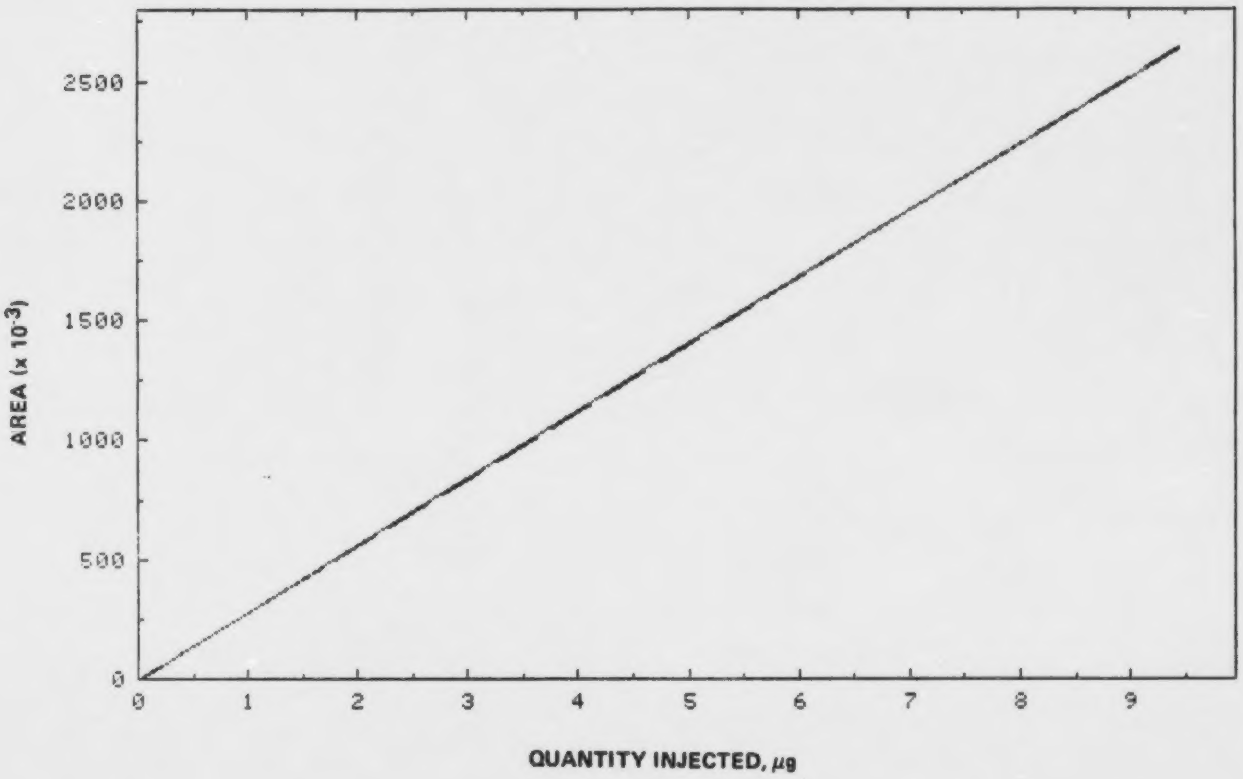

Figure C-25. Calibration curve for the determination of tetramethylthiuram disulfide by HPLC/UV.

Range: 0.047 - 9.4 µg
Correlation coefficient: 0.999
Slope: $2.8 \times 10^{+2}$
y-Intercept: -2.7

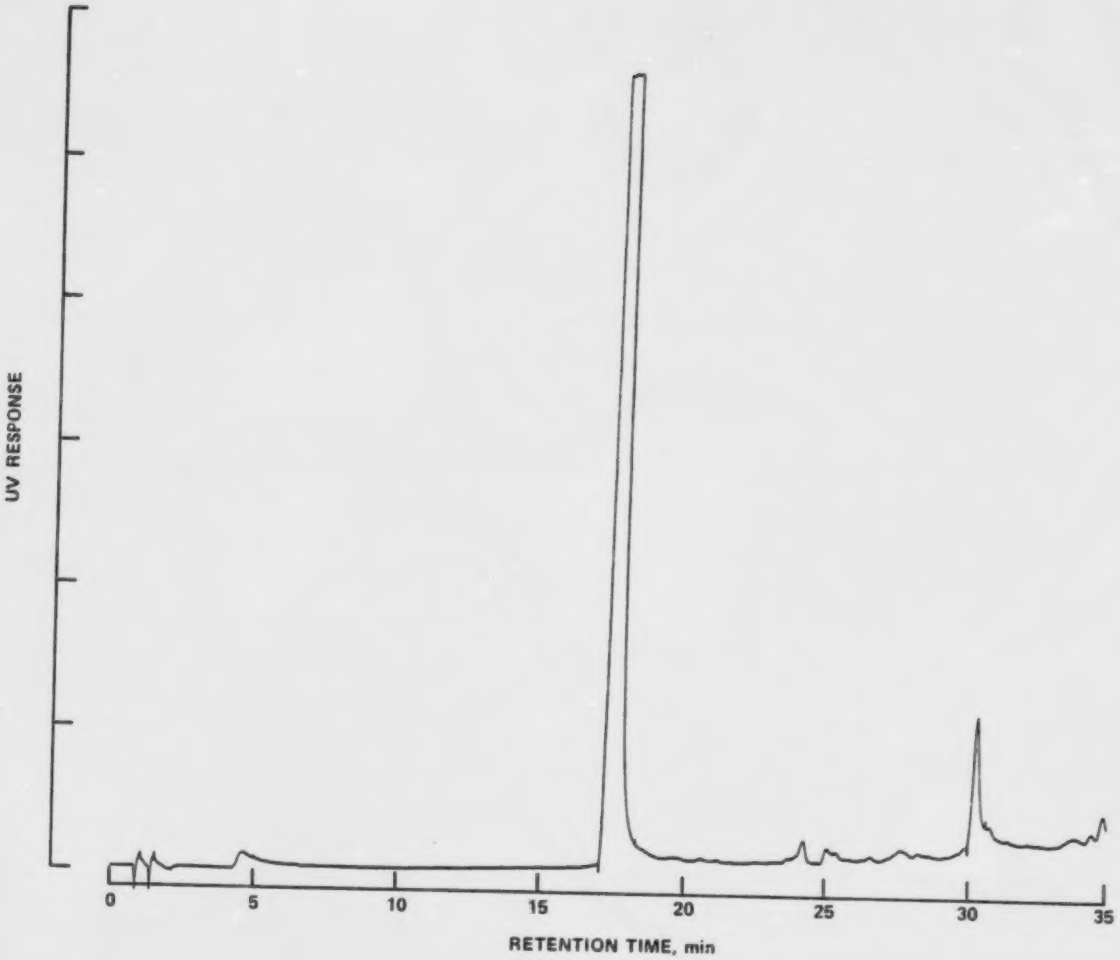

Figure C-26. Chromatogram by HPLC/UV for 4-chloro-m-cresol.

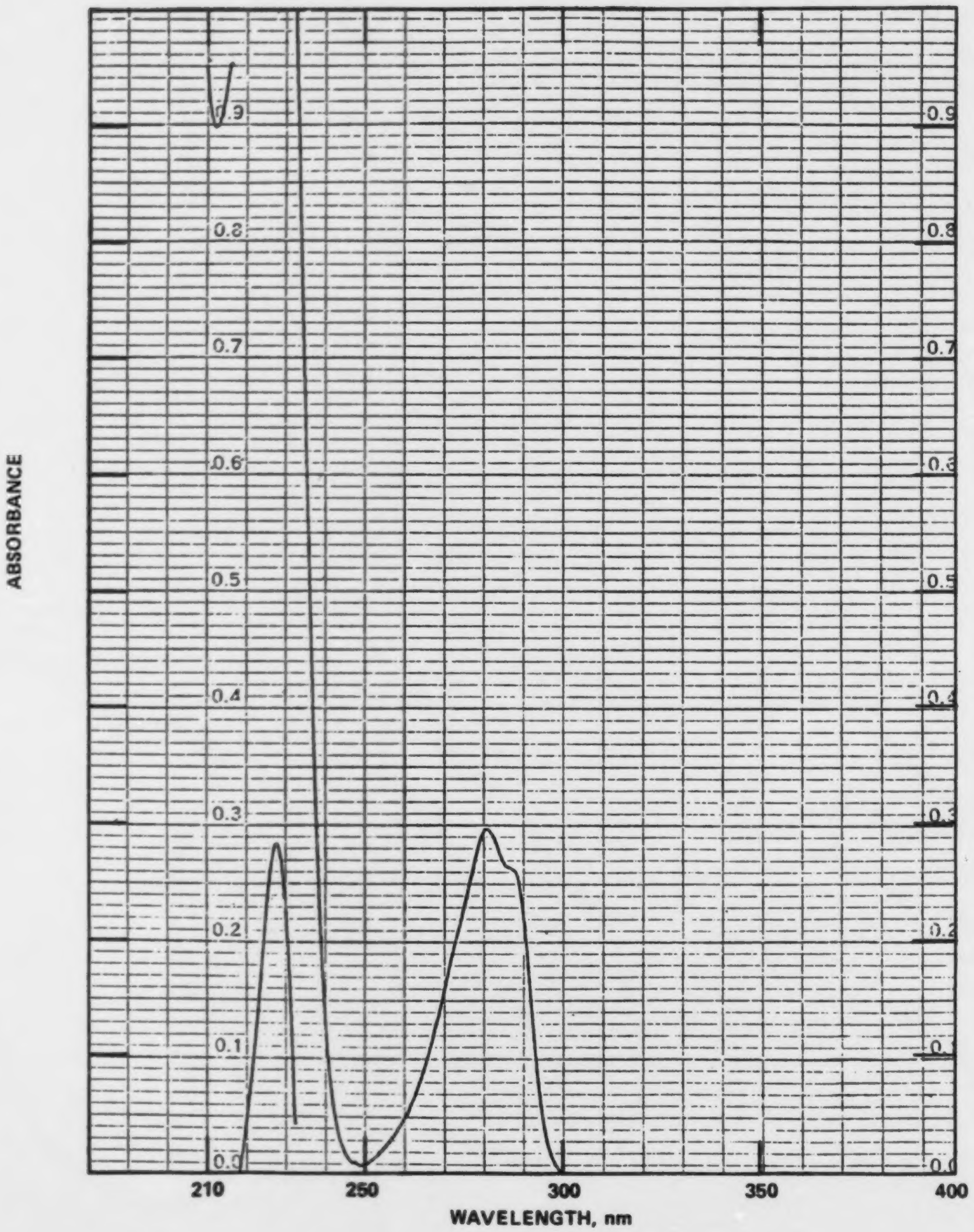

Figure C-27. UV spectrum of 4-chloro-*m*-cresol.

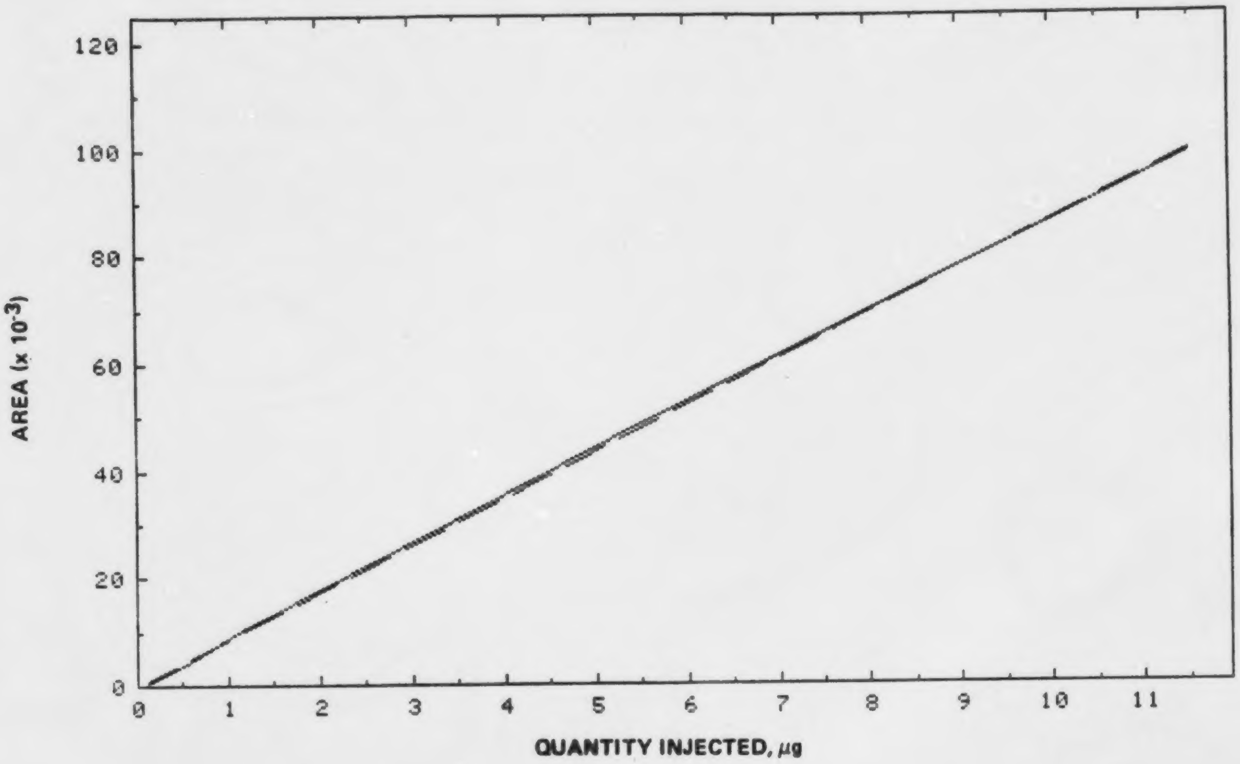

Figure C-28. Calibration curve for the determination of 4-chloro-m-cresol by HPLC/UV.

Range: 0.57 - 12 µg
Correlation coefficient: 0.999
Slope: 8.6
y-Intercept: -1.3

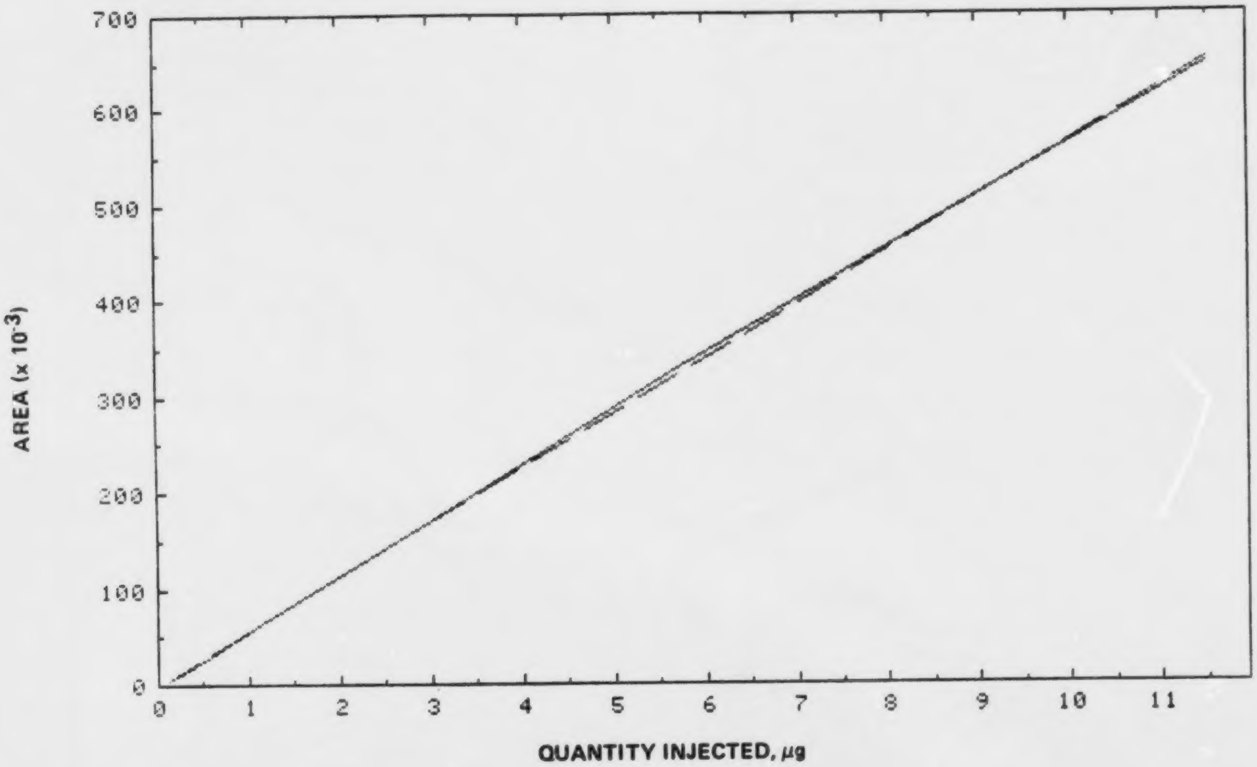

Figure C-29. Calibration curve for the determination of 4-chloro-m-cresol by HPLC/UV(280nm).

Range: 0.57 - 12 µg
Correlation coefficient: 0.999
Slope: $5.7 \times 10^{+1}$
y-Intercept: -1.1

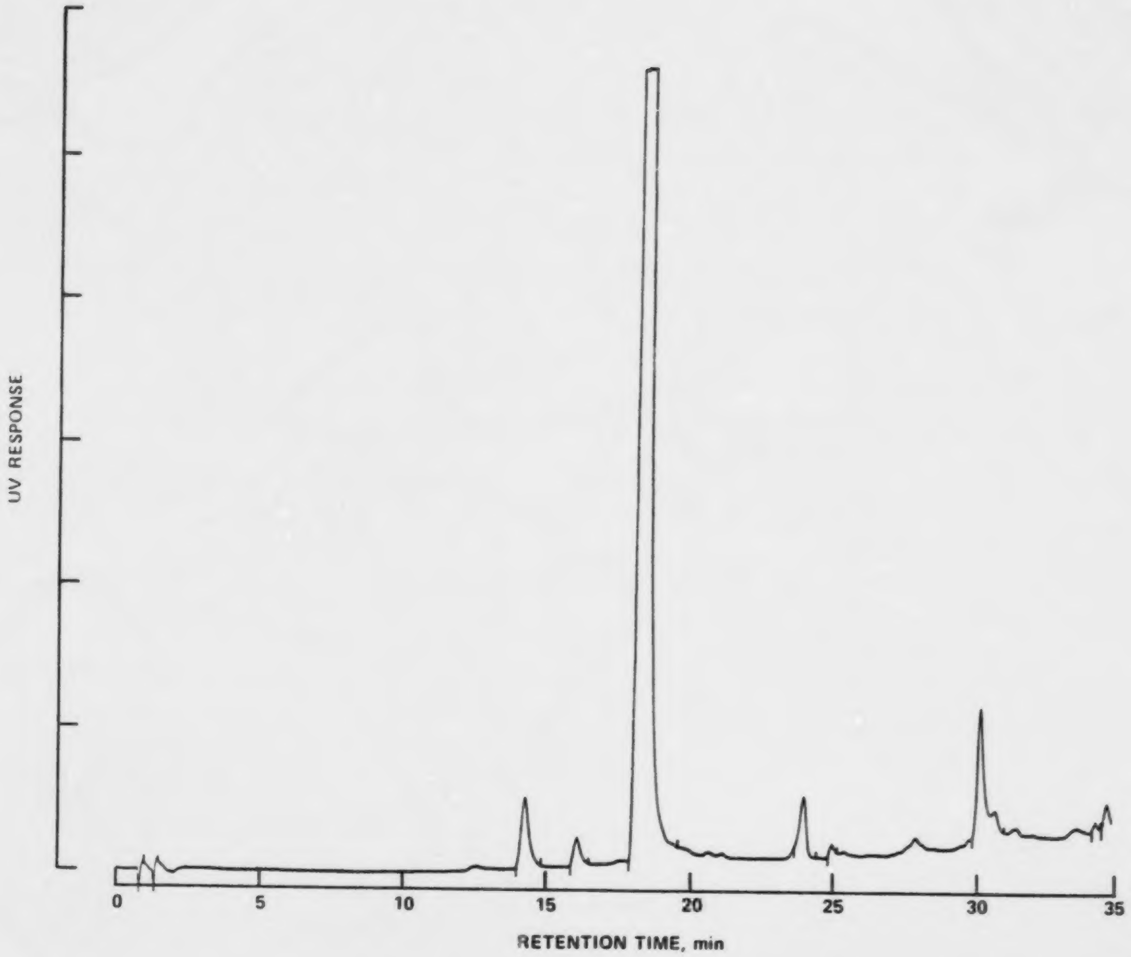

Figure C-30. Chromatogram by HPLC/UV for 2,4-dichlorophenol.

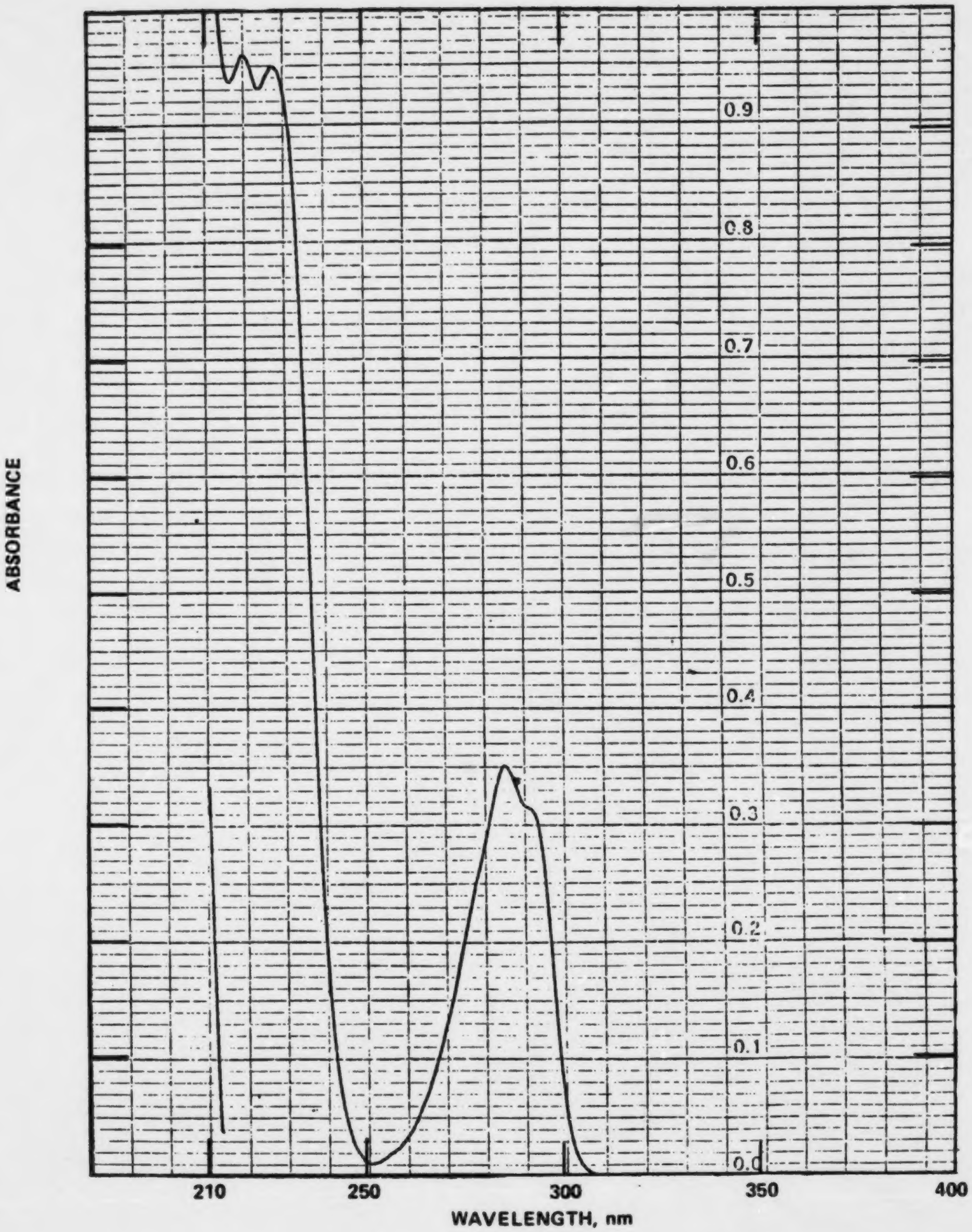

Figure C-31. UV spectrum of 2,4-dichlorophenol.

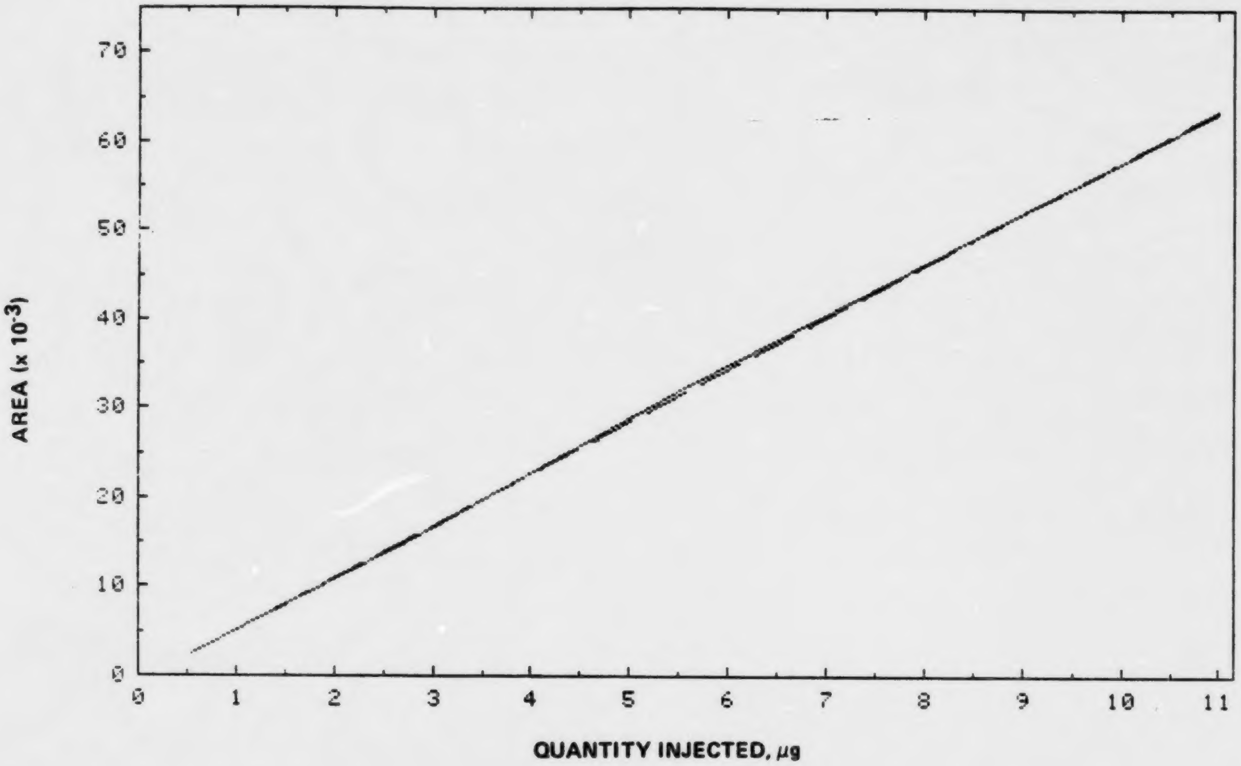

Figure C-32. Calibration curve for the determination of 2,4-dichlorophenol by HPLC/UV.

Range: 0.55 - 11 µg
Correlation coefficient: 0.999
Slope: 5.9
y-Intercept: -8.3×10^{-1}

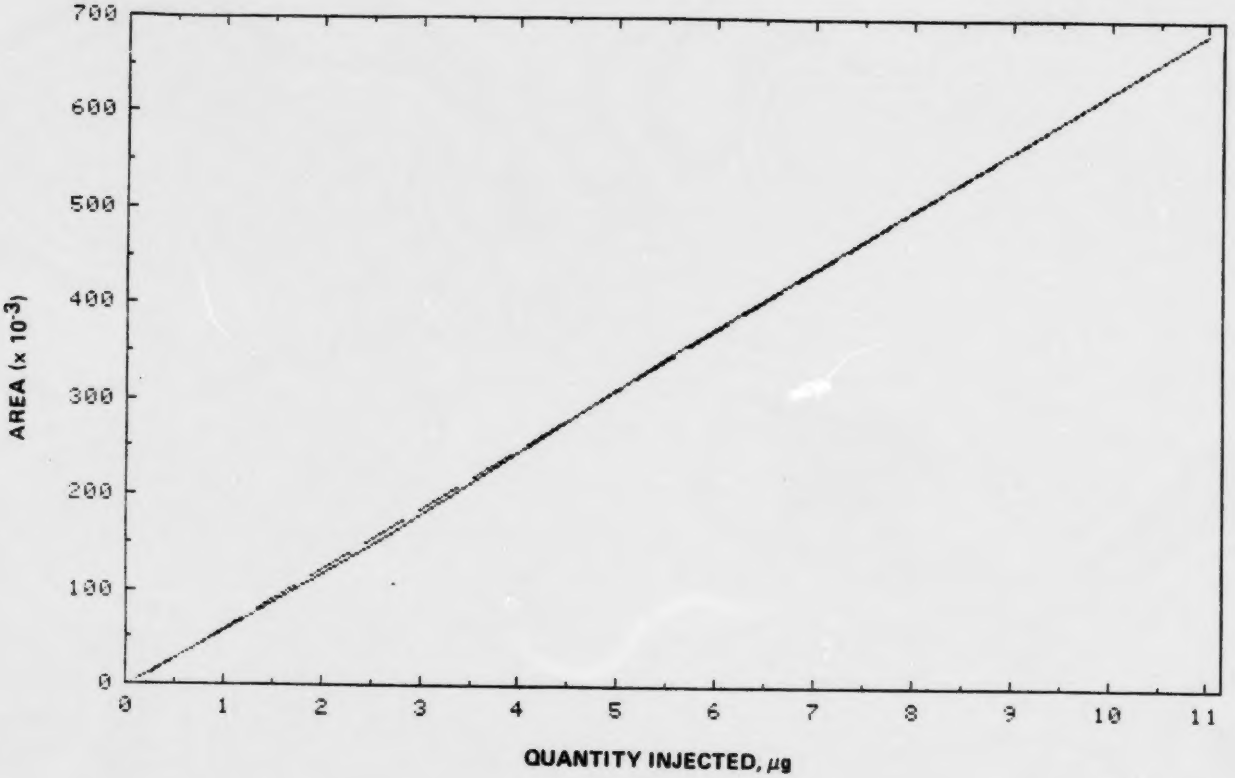

Figure C-33. Calibration curve for the determination of 2,4-dichlorophenol by HPLC/UV(280nm).

Range: 0.55 - 11 μg
Correlation coefficient: 0.999
Slope: $6.3 \times 10^{+1}$
y-Intercept: -4.2

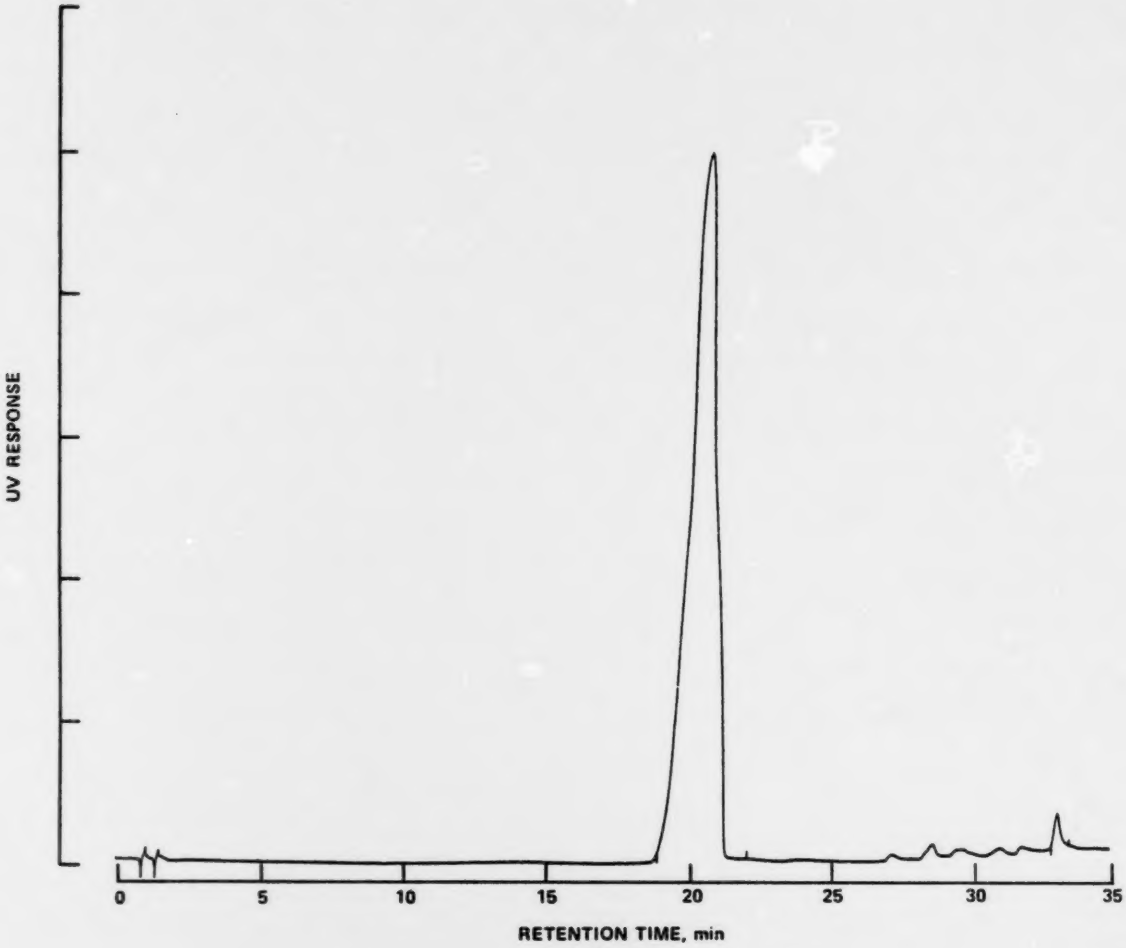

Figure C-34. Chromatogram by HPLC/UV for 3-(alpha-acetonylbenzyl)-4-hydroxycoumarin.

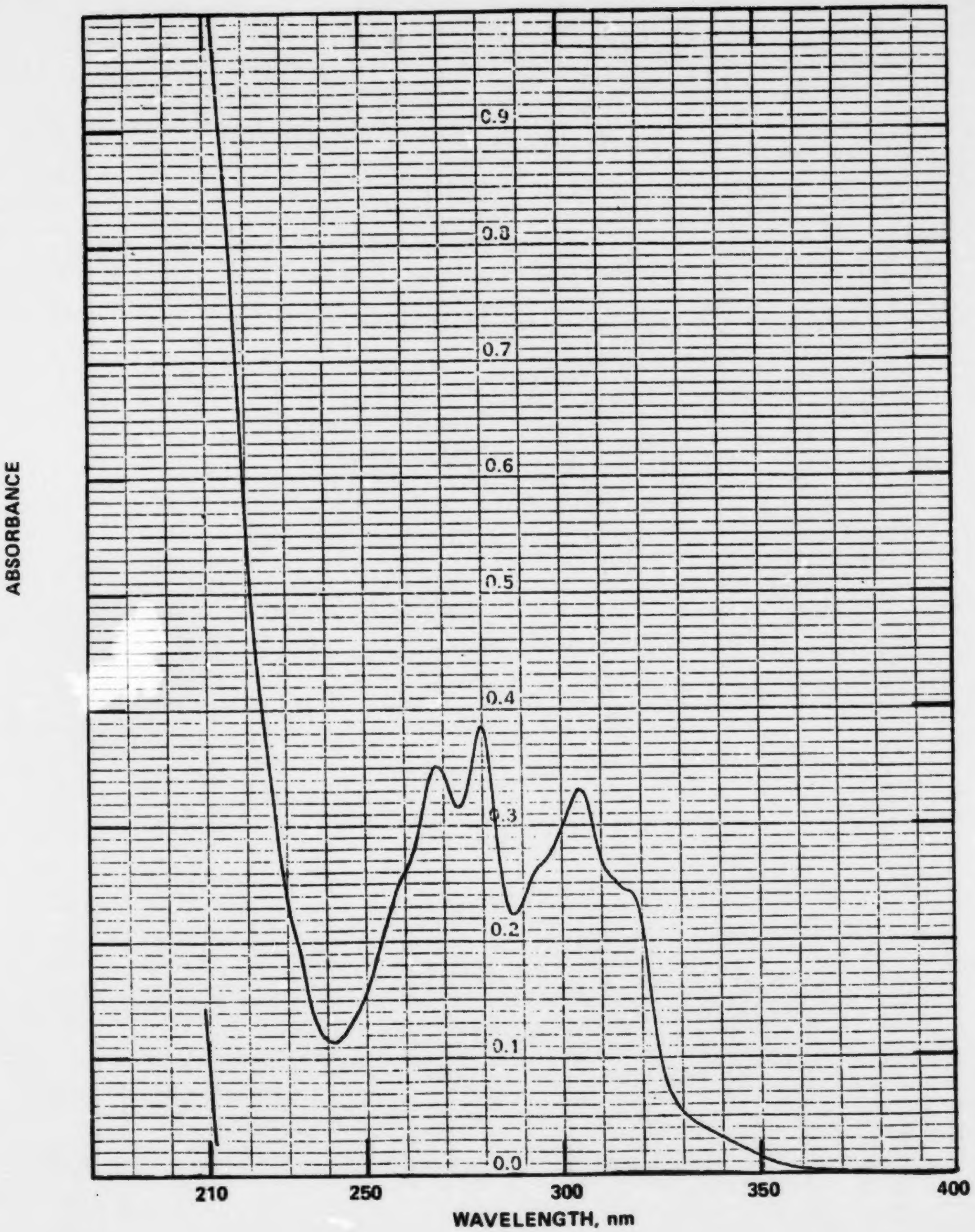

Figure C-35. UV spectrum of 3-(alpha-acetonylbenzyl)-4-hydroxycoumarin.

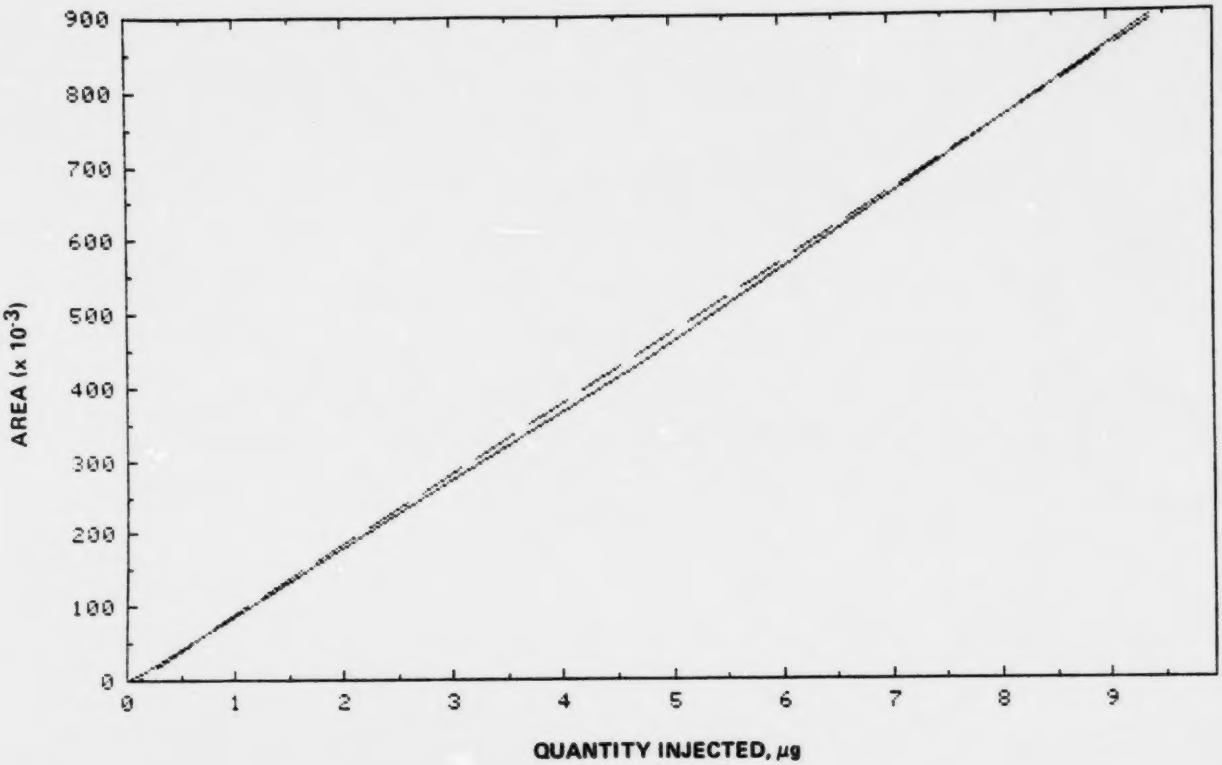

Figure C-36. Calibration curve for the determination of 3-(alpha-acetonylbenzyl)-4-hydroxycoumarin by HPLC/UV.

Range: 0.47 - 9.4 µg
Correlation coefficient: 0.999
Slope: $9.5 \times 10^{+1}$
y-Intercept: -7.8

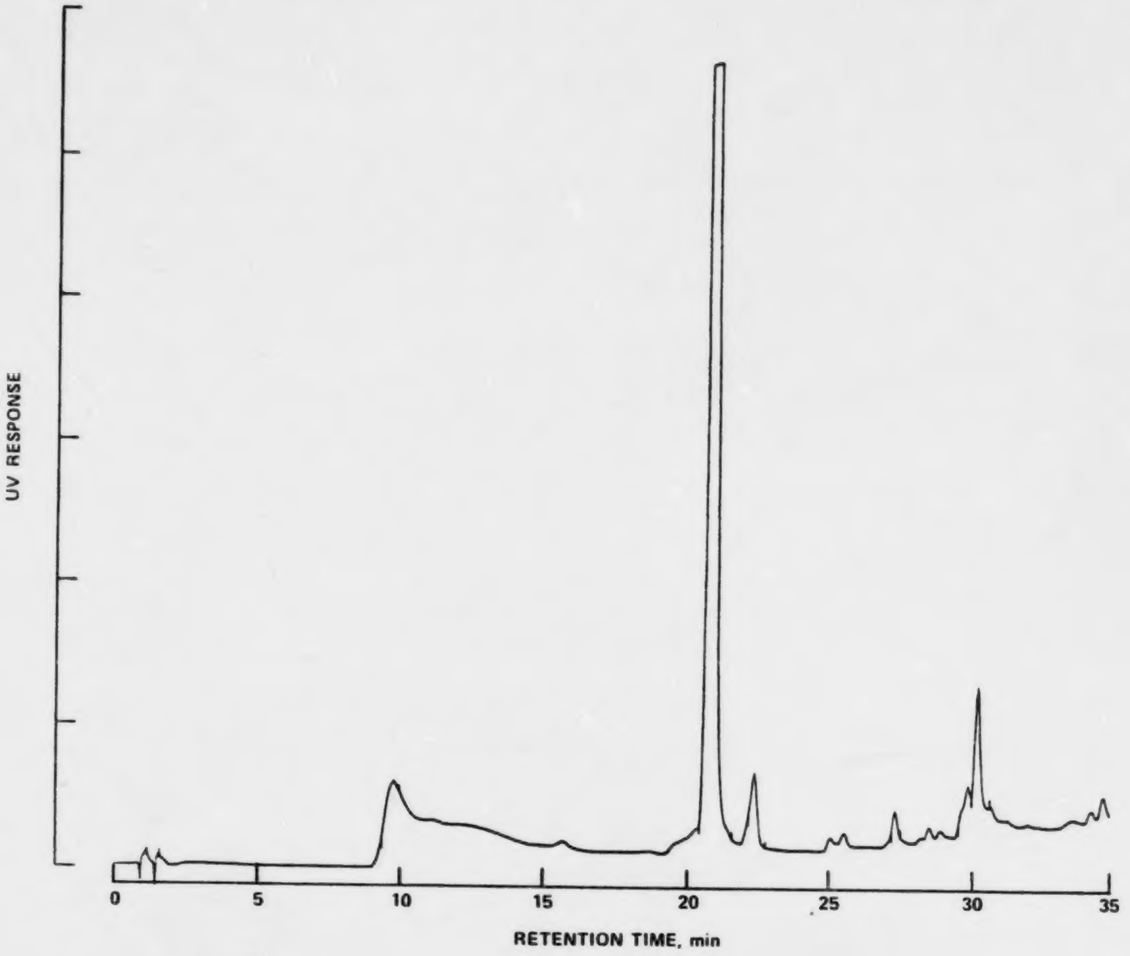

Figure C-37. Chromatogram by HPLC/UV for 2,4,6-trichlorophenol.

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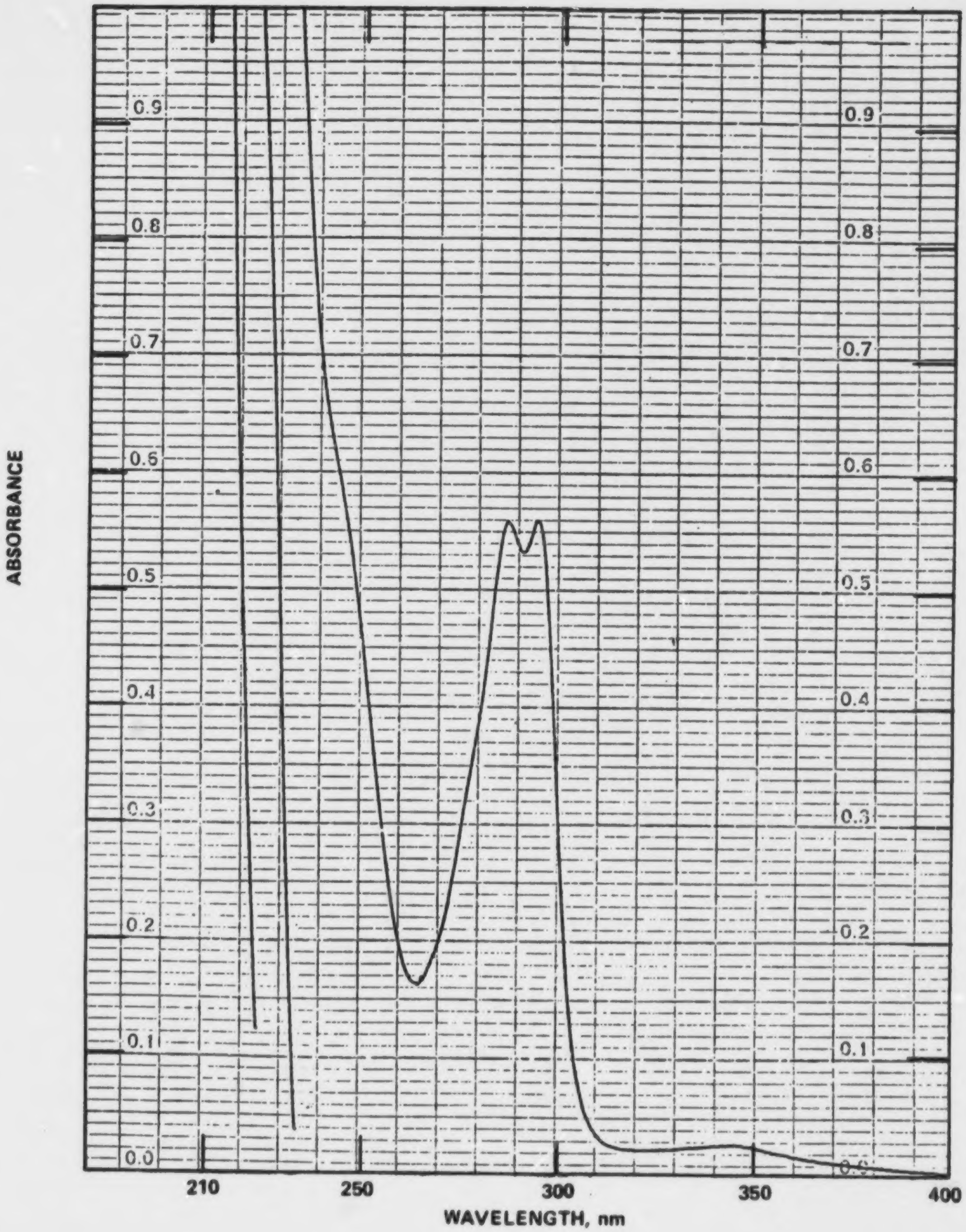

Figure C-38. UV spectrum of 2,4,6-trichlorophenol.

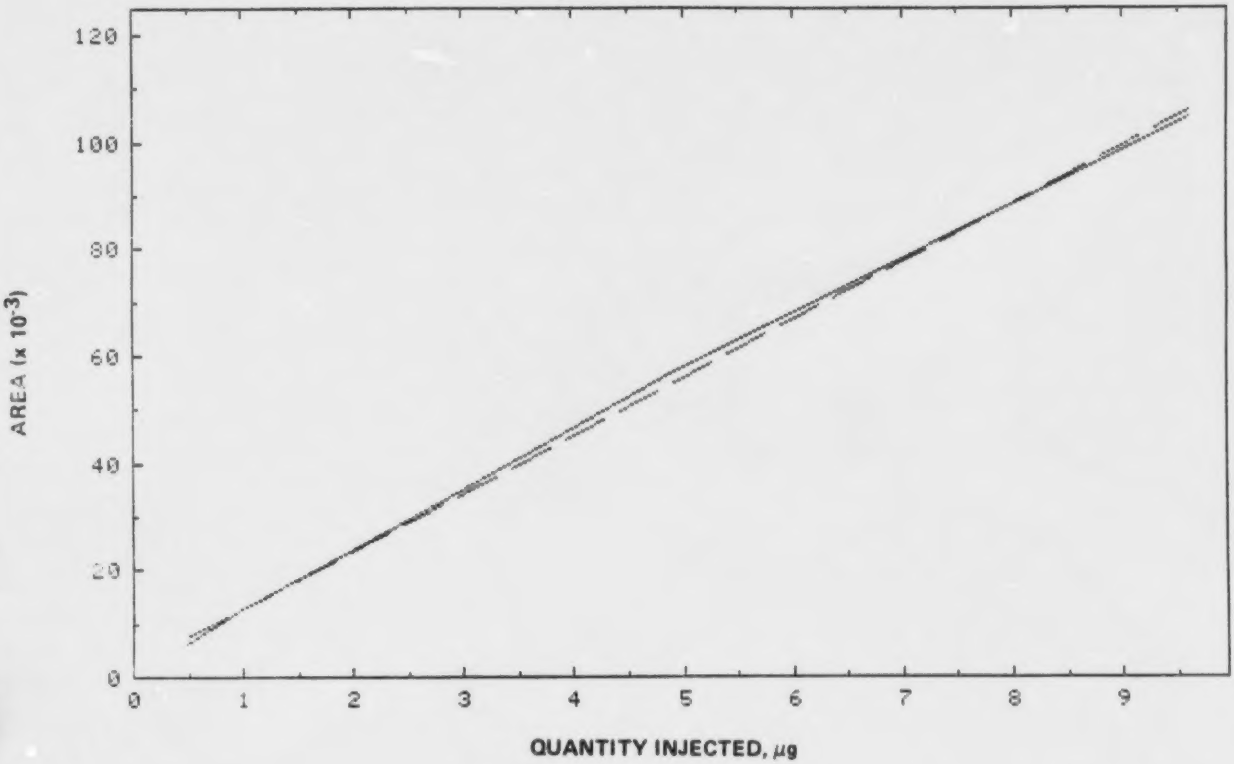

Figure C-39. Calibration curve for the determination of 2,4,6-trichlorophenol by HPLC/UV.

Range: 0.48 - 9.6 μg
Correlation coefficient: 0.999
Slope: $1.1 \times 10^{+1}$
y-Intercept: 2.0

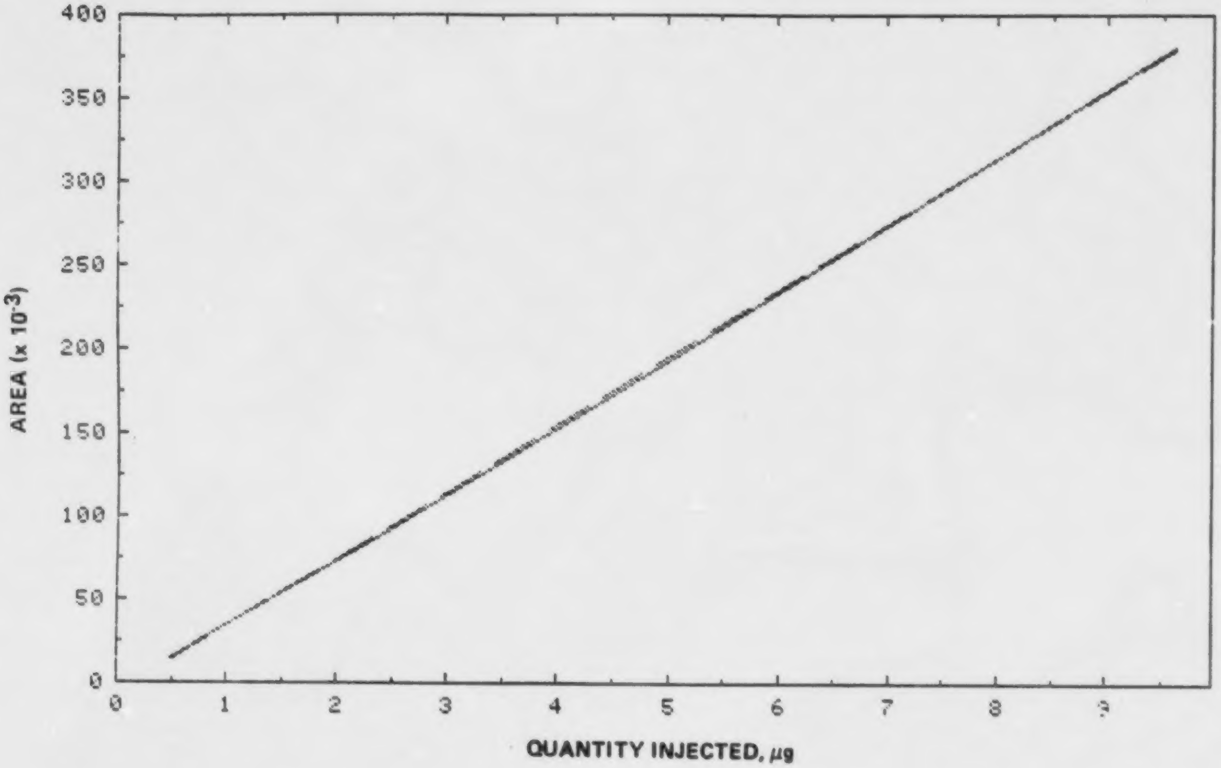

Figure C-40. Calibration curve for the determination of 2,4,6-trichlorophenol by HPLC/UV(280nm).

Range: 0.48 - 9.6 μg
Correlation coefficient: 0.999
Slope: $4.0 \times 10^{+1}$
y-Intercept: -6.2

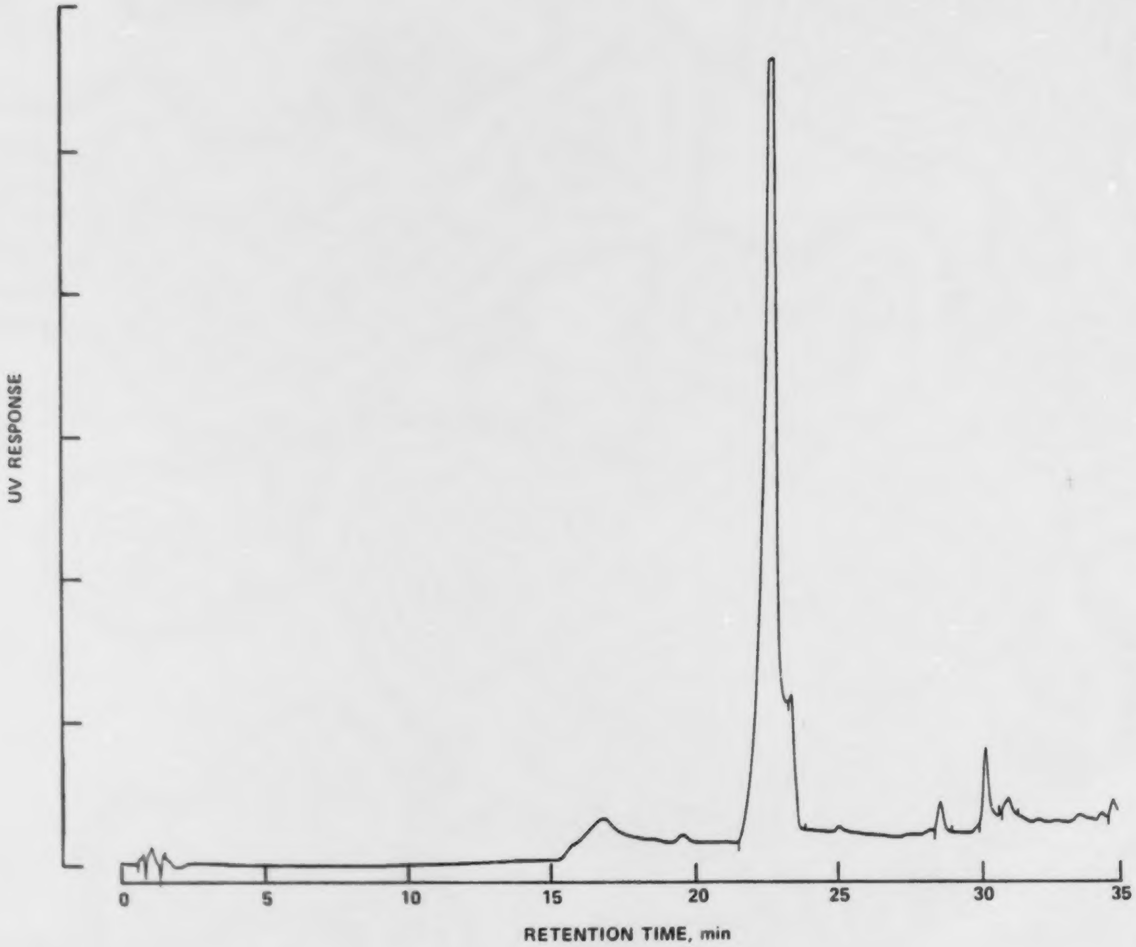

Figure C-41. Chromatogram by HPLC/UV for 2,3,4,6-tetrachlorophenol.

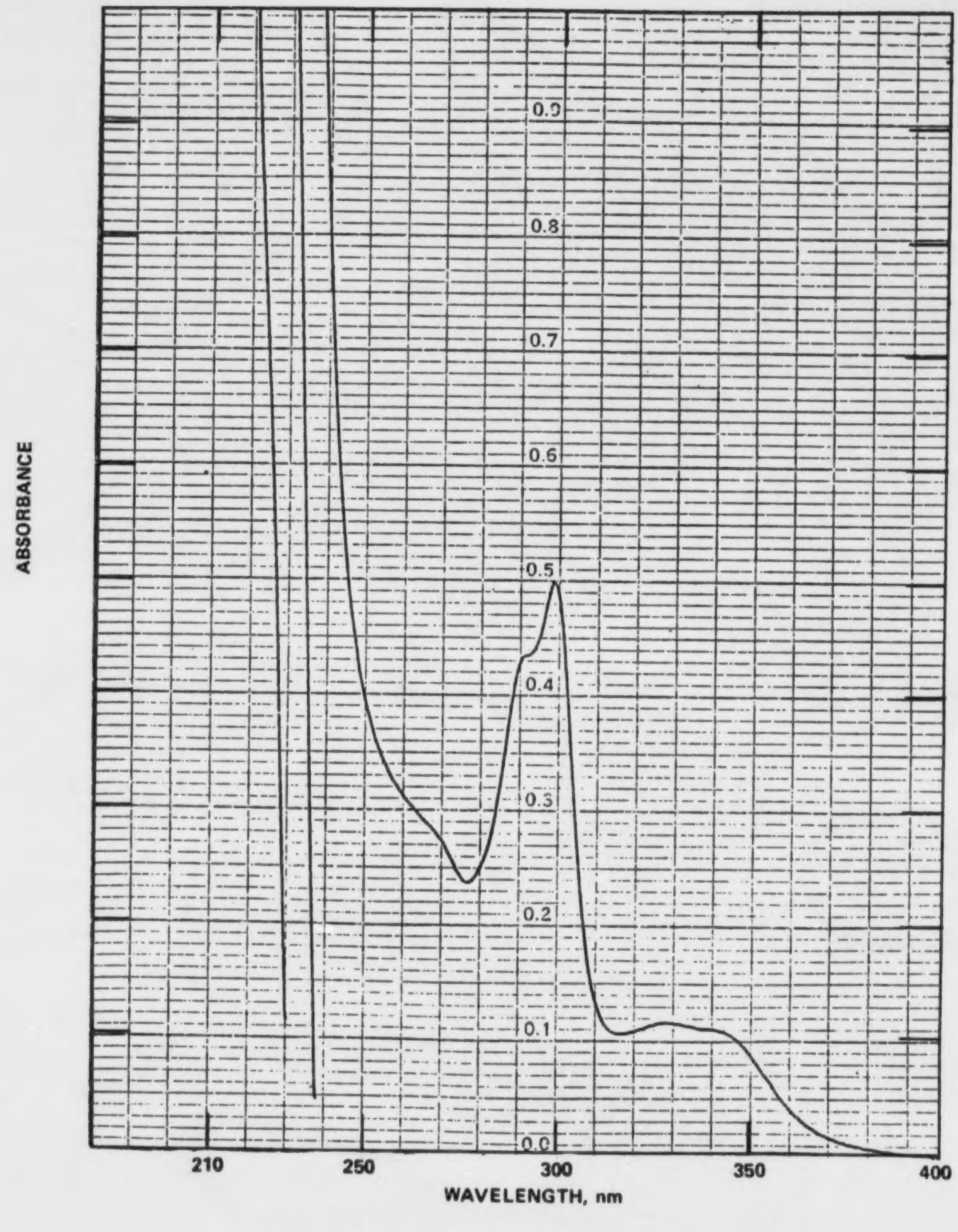

Figure C-42. UV spectrum of 2,3,4,6-tetrachlorophenol.

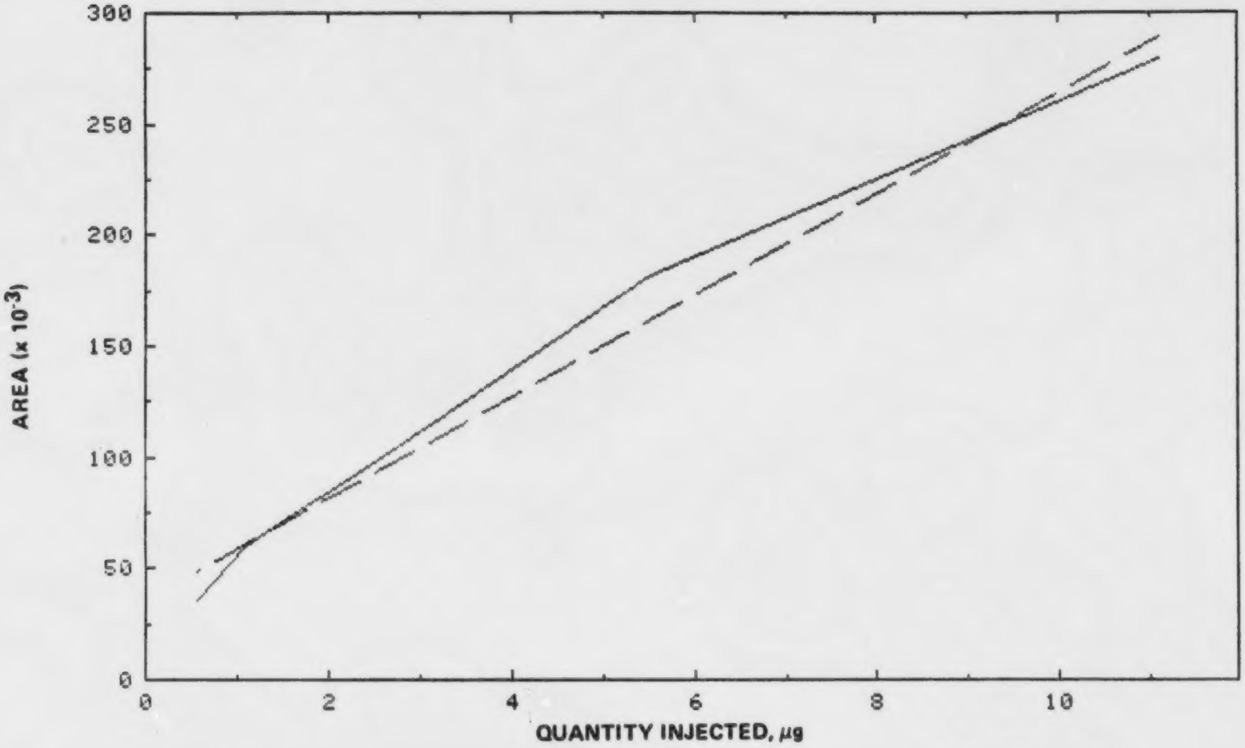

Figure C-43. Calibration curve for the determination of 2,3,4,6-tetrachlorophenol by HPLC/UV.

Range: 0.55 - 11 μg
Correlation coefficient: 0.990
Slope: $2.3 \times 10^{+1}$
y-Intercept: $3.6 \times 10^{+1}$

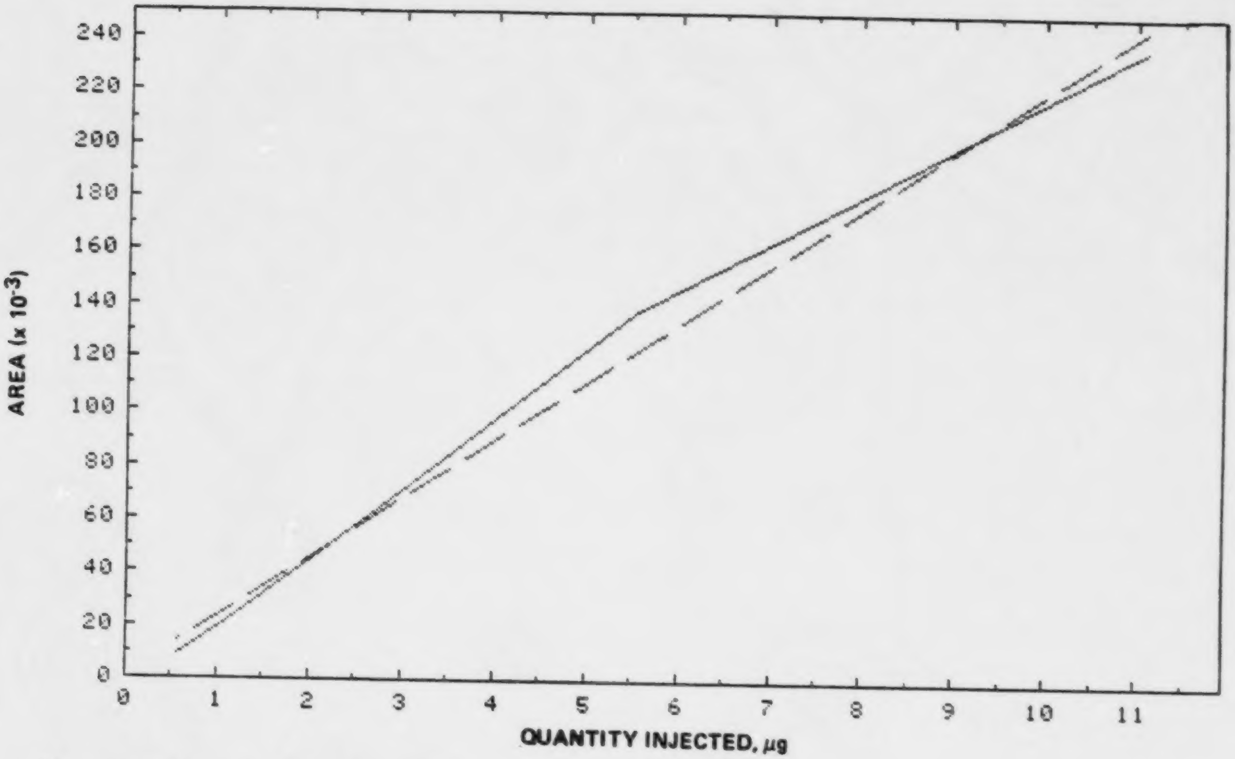

Figure C-44. Calibration curve for the determination of 2,3,4,6-tetrachlorophenol by HPLC/UV(280nm).

Range: 1.1 - 11 µg
Correlation coefficient: 0.995
Slope: $2.2 \times 10^{+1}$
y-Intercept: 1.6

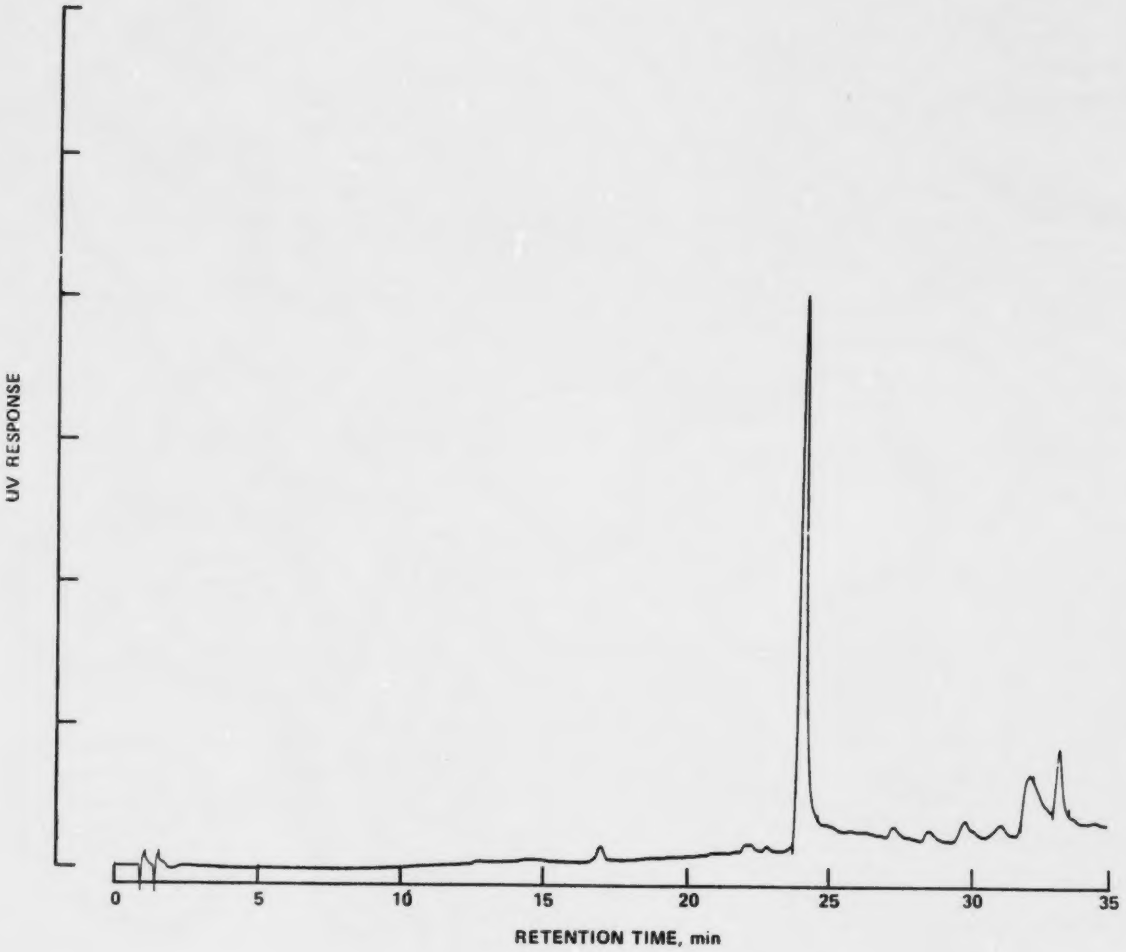

Figure C-45. Chromatogram by HPLC/UV for reserpine.

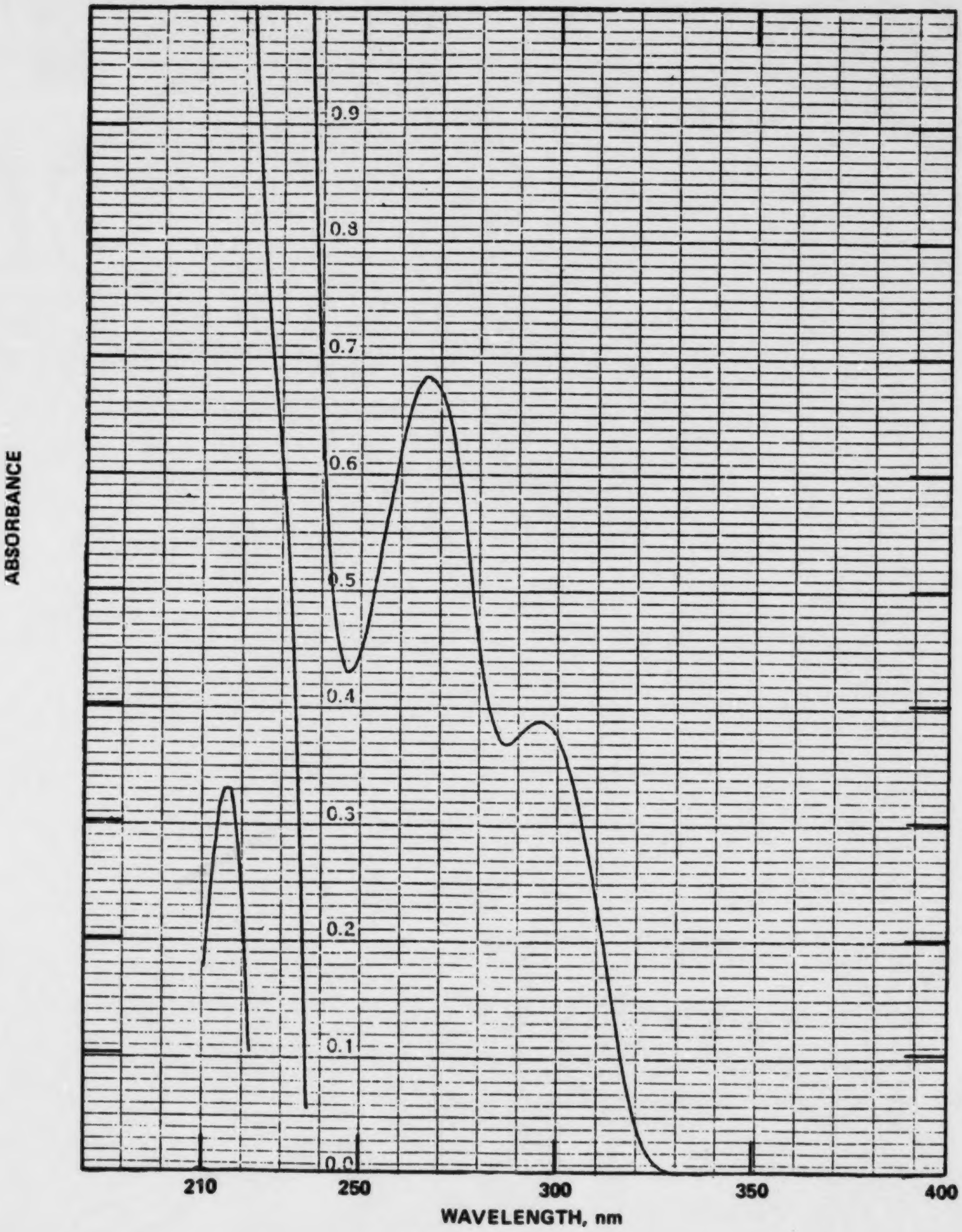

Figure C-46. UV spectrum of reserpine.

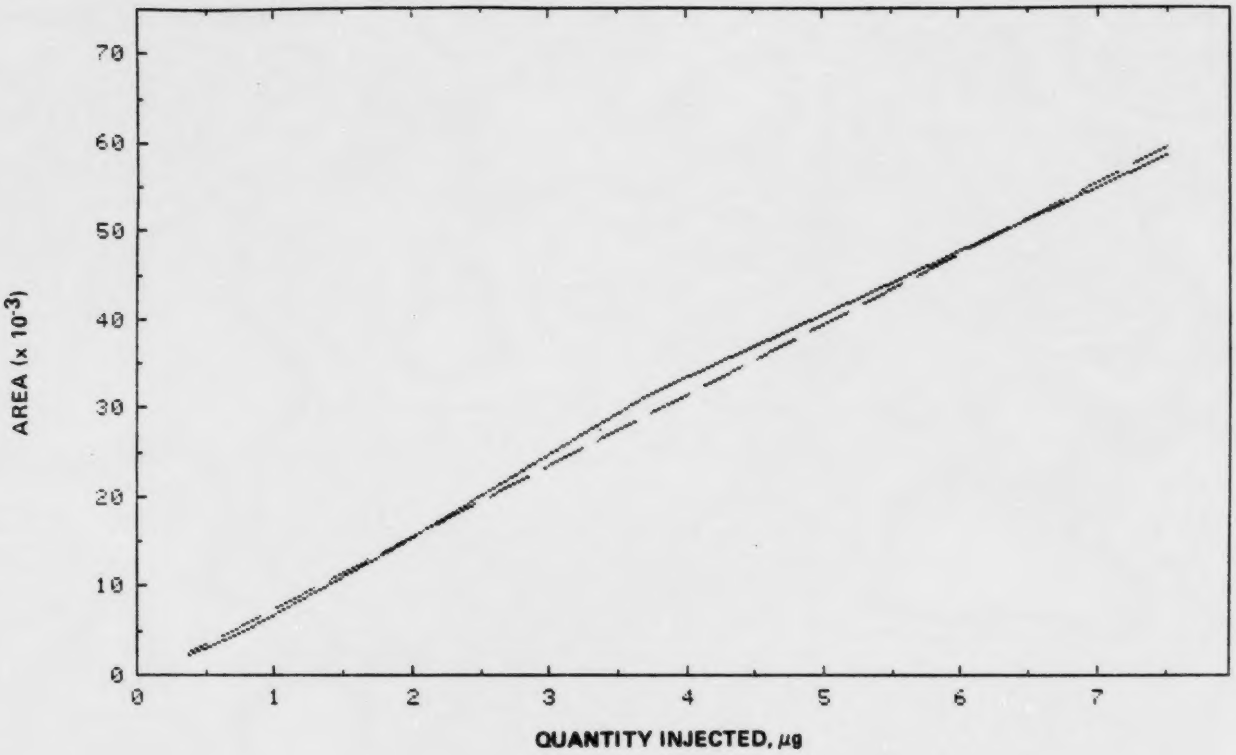

Figure C-47. Calibration curve for the determination of reserpine by HPLC/UV.

Range: 0.37 - 7.5 μg
Correlation coefficient: 0.998
Slope: 8.0
y-Intercept: -4.6×10^{-1}

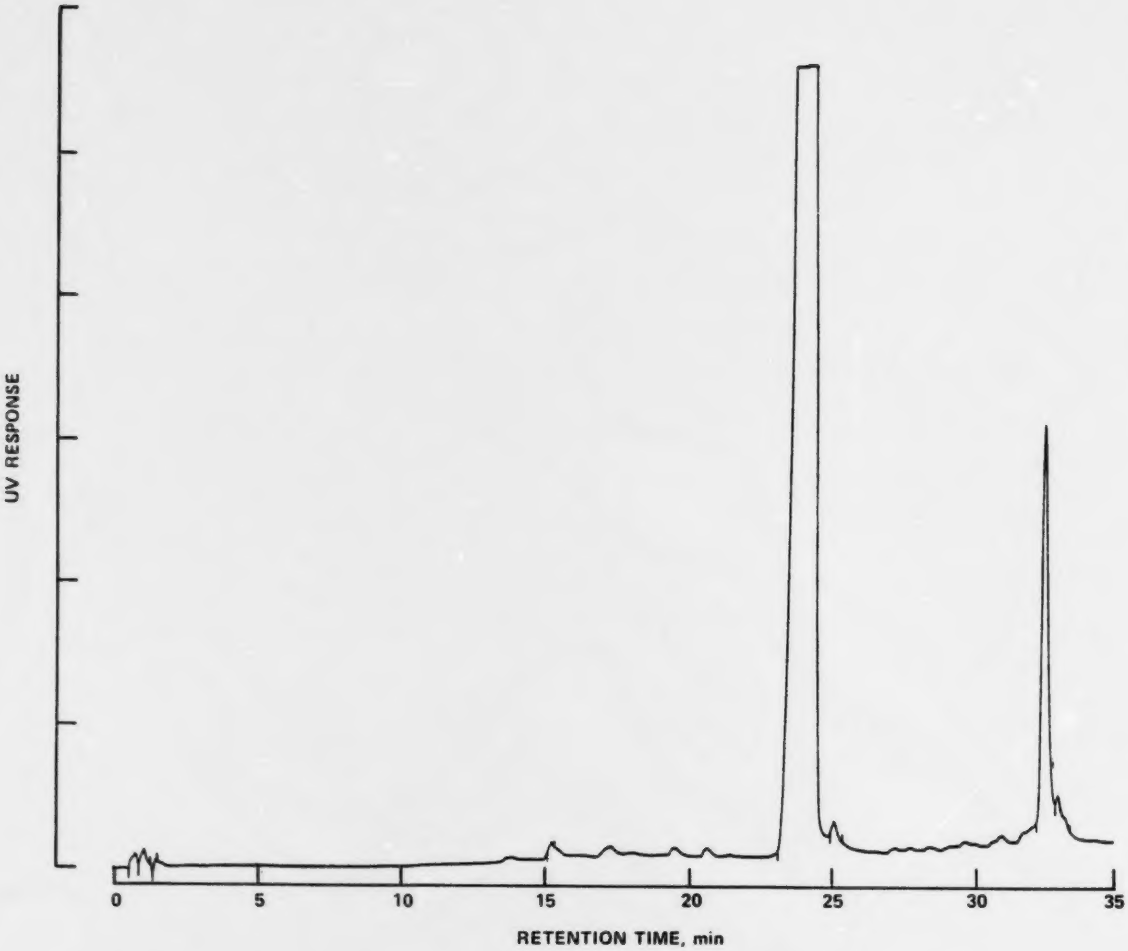

Figure C-48. Chromatogram by HPLC/UV for chlorambucil.

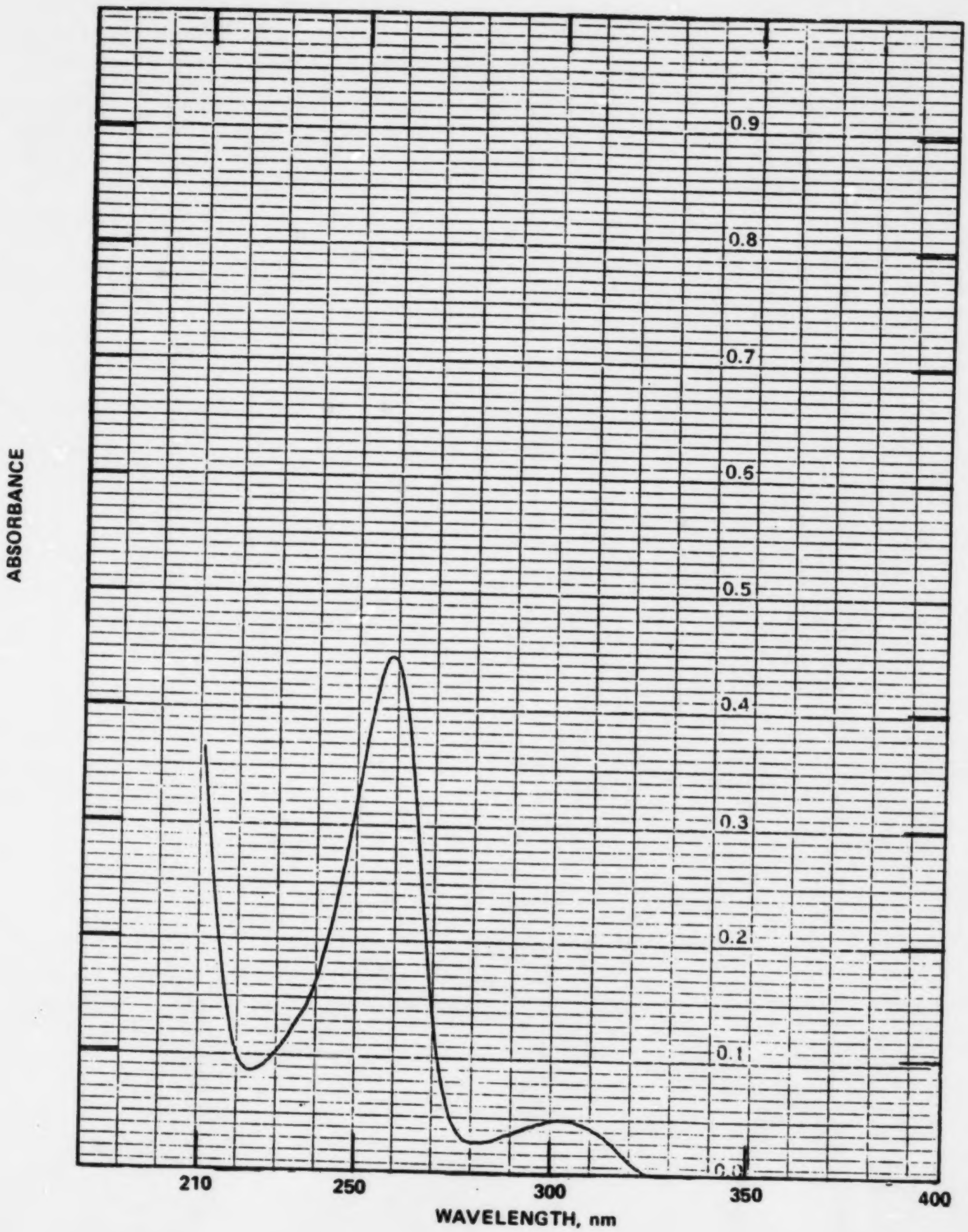

Figure C-49. UV spectrum of chlorambucil.

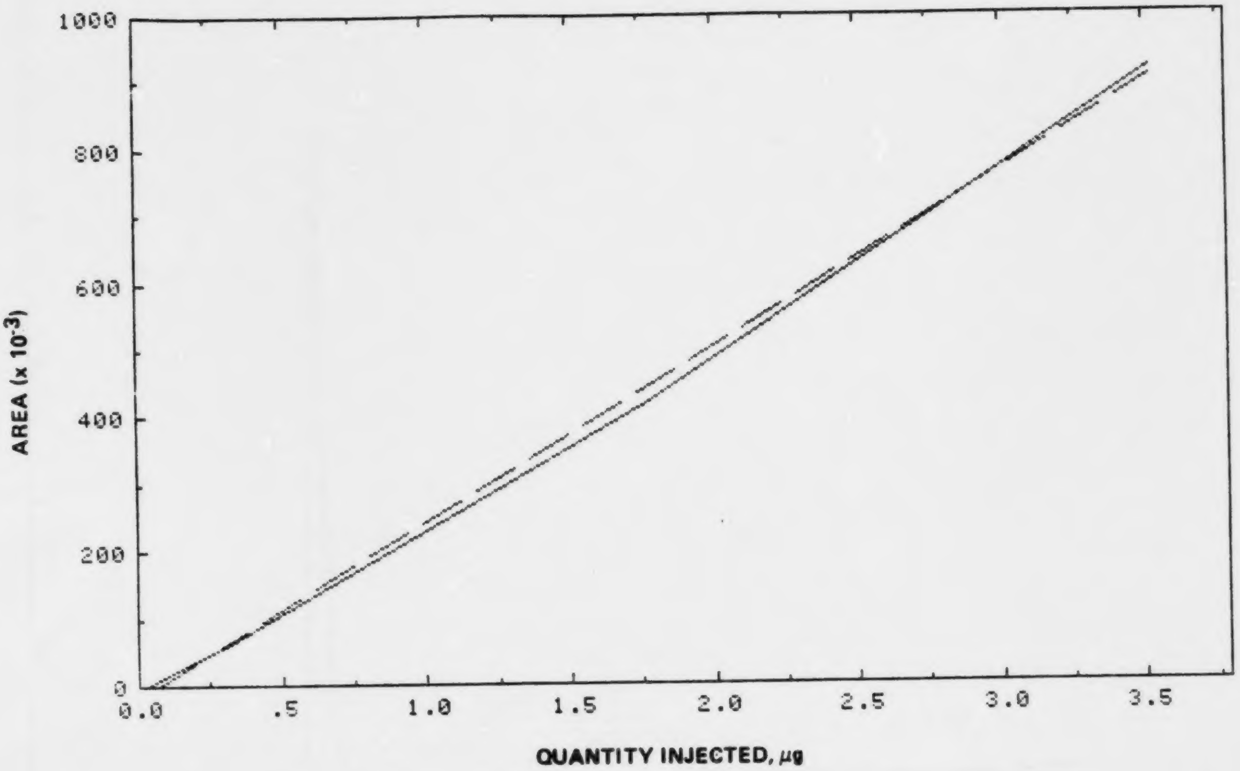

Figure C-50. Calibration curve for the determination of chlorambucil by HPLC/UV.

Range: 0.35 - 3.5 µg
Correlation coefficient: 0.999
Slope: $2.6 \times 10^{+2}$
y-Intercept: $-2.0 \times 10^{+1}$

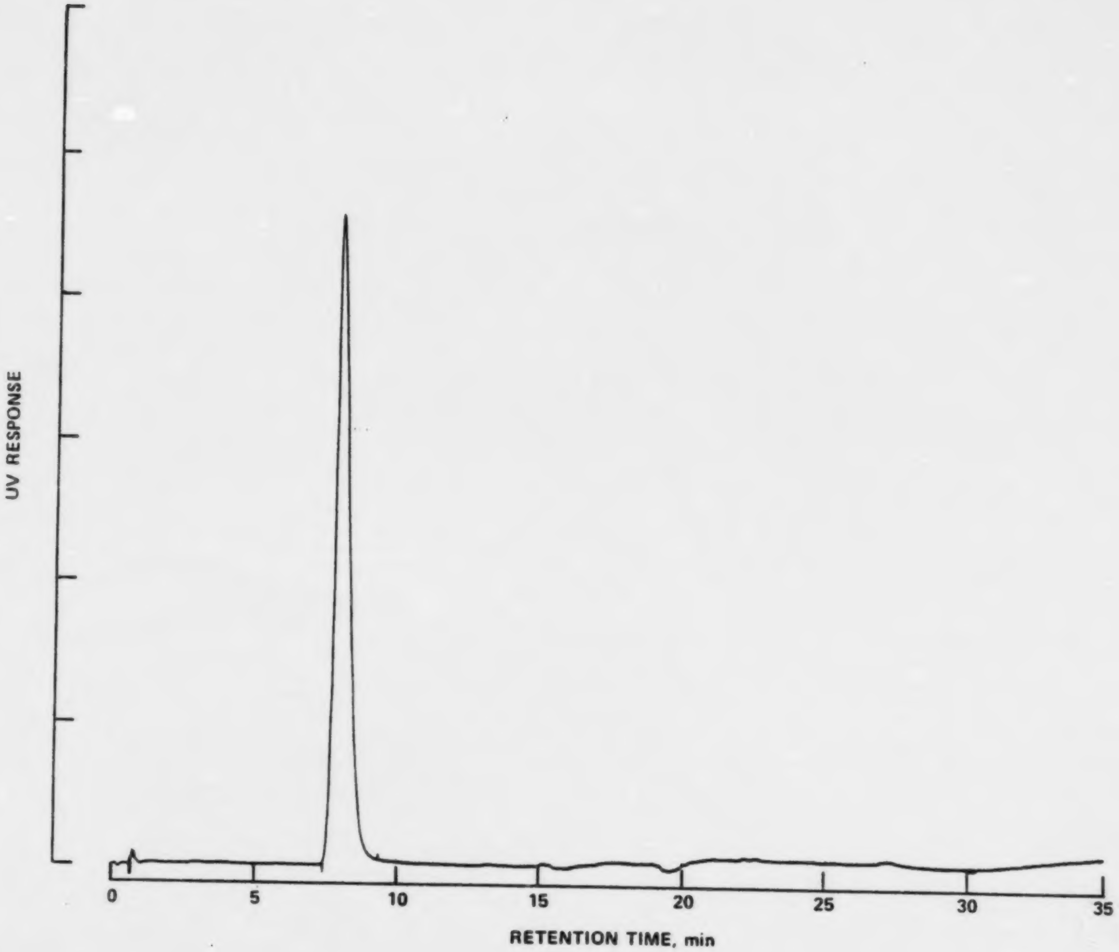

Figure C-51. Chromatogram by HPLC/UV for 2,4-dichlorophenoxyacetic acid.

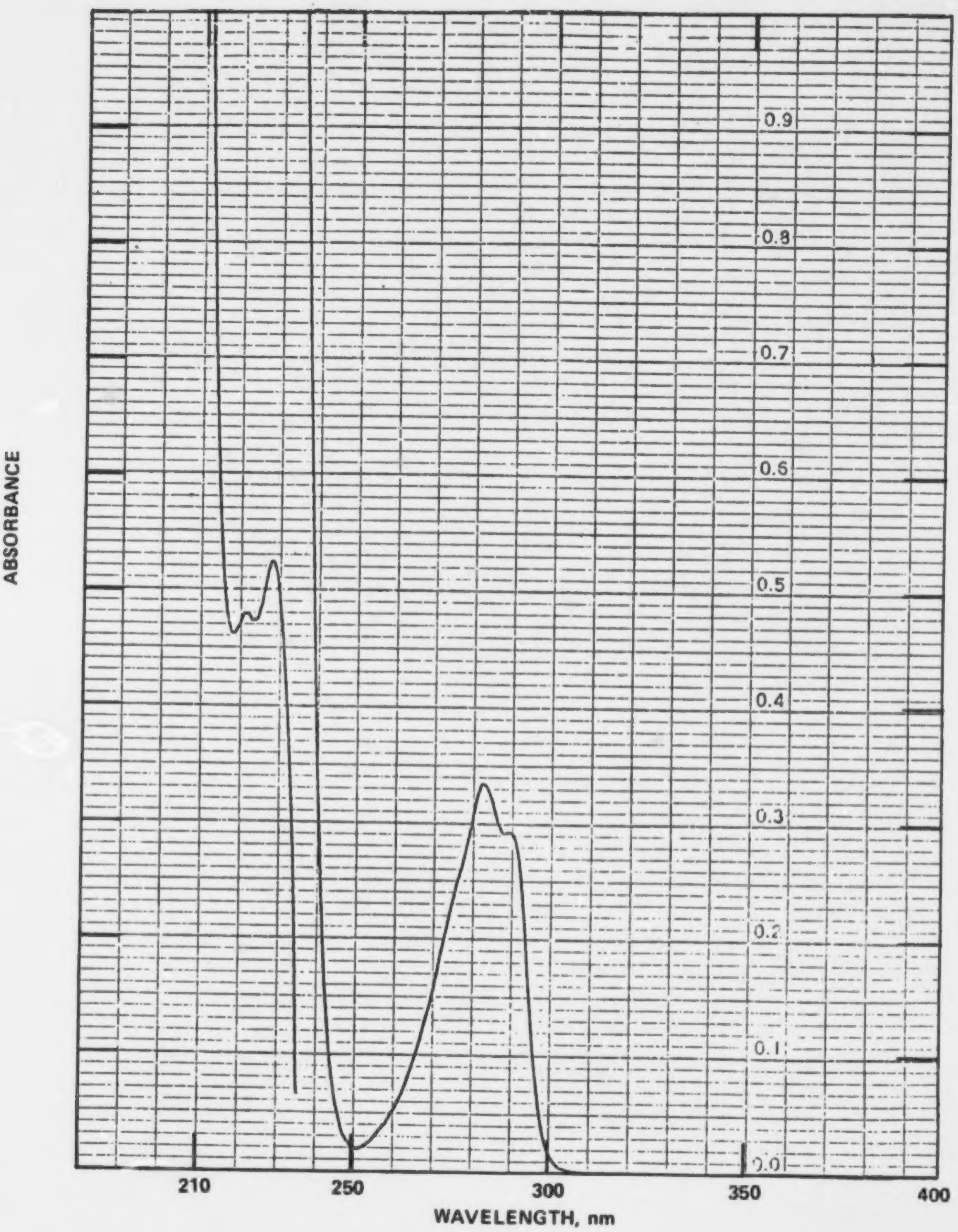

Figure C-52. UV spectrum of 2,4-dichlorophenoxyacetic acid.

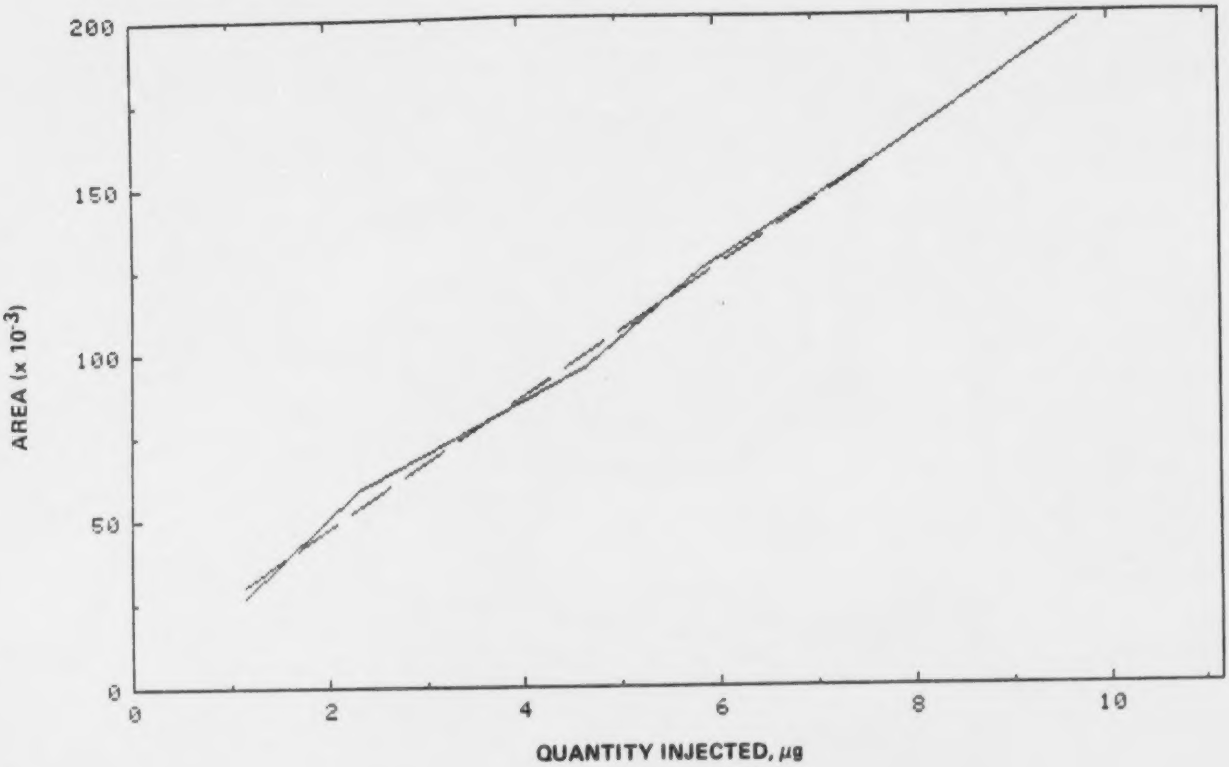

Figure C-53. Calibration curve for the determination of 2,4-dichlorophenoxyacetic acid by HPLC/UV.

Range: 1.2 - 9.7 µg
Correlation coefficient: 0.998
Slope: $2.0 \times 10^{+1}$
y-Intercept: 7.3

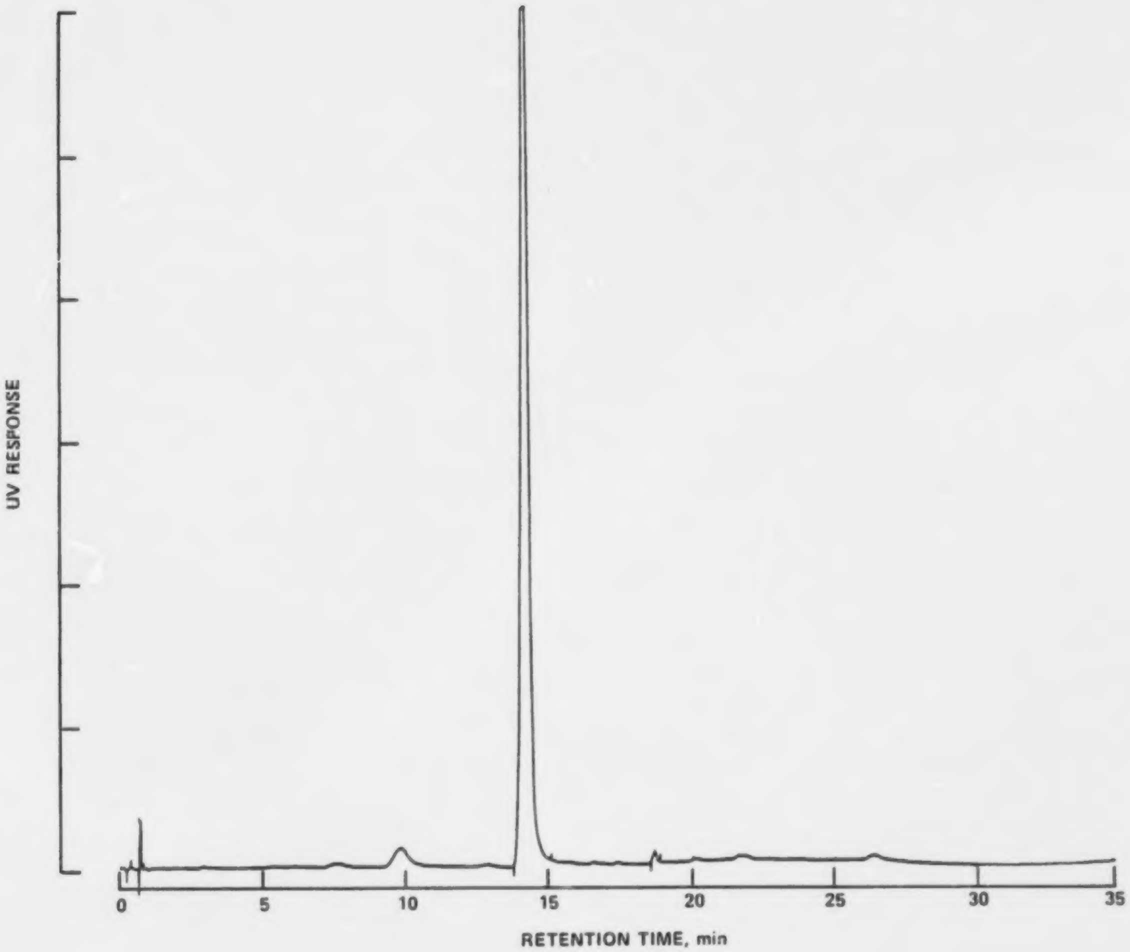

Figure C-54. Chromatogram by HPLC/UV for 2,4,5-trichlorophenoxyacetic acid.

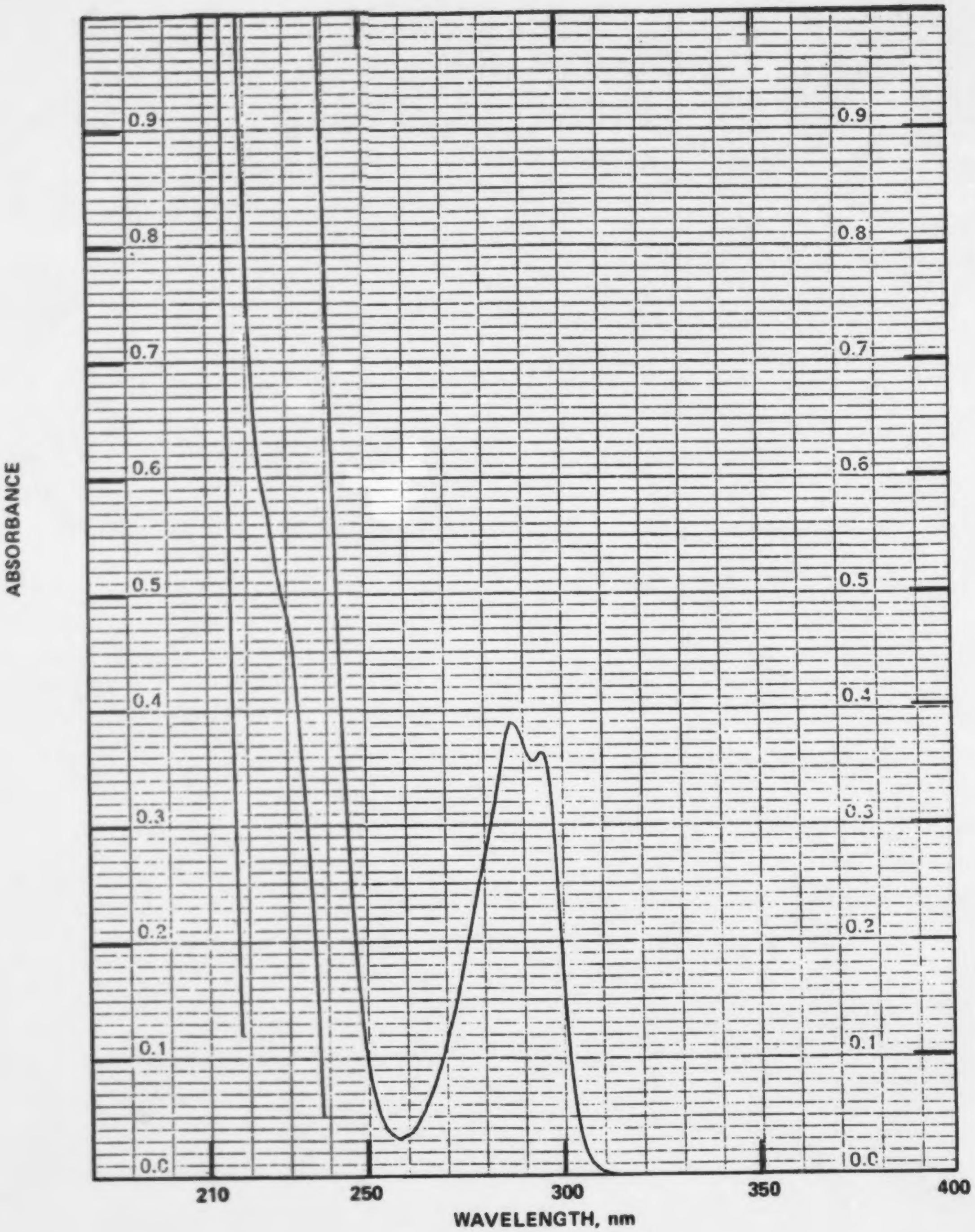

Figure C-55. UV spectrum of 2,4,5-trichlorophenoxyacetic acid.

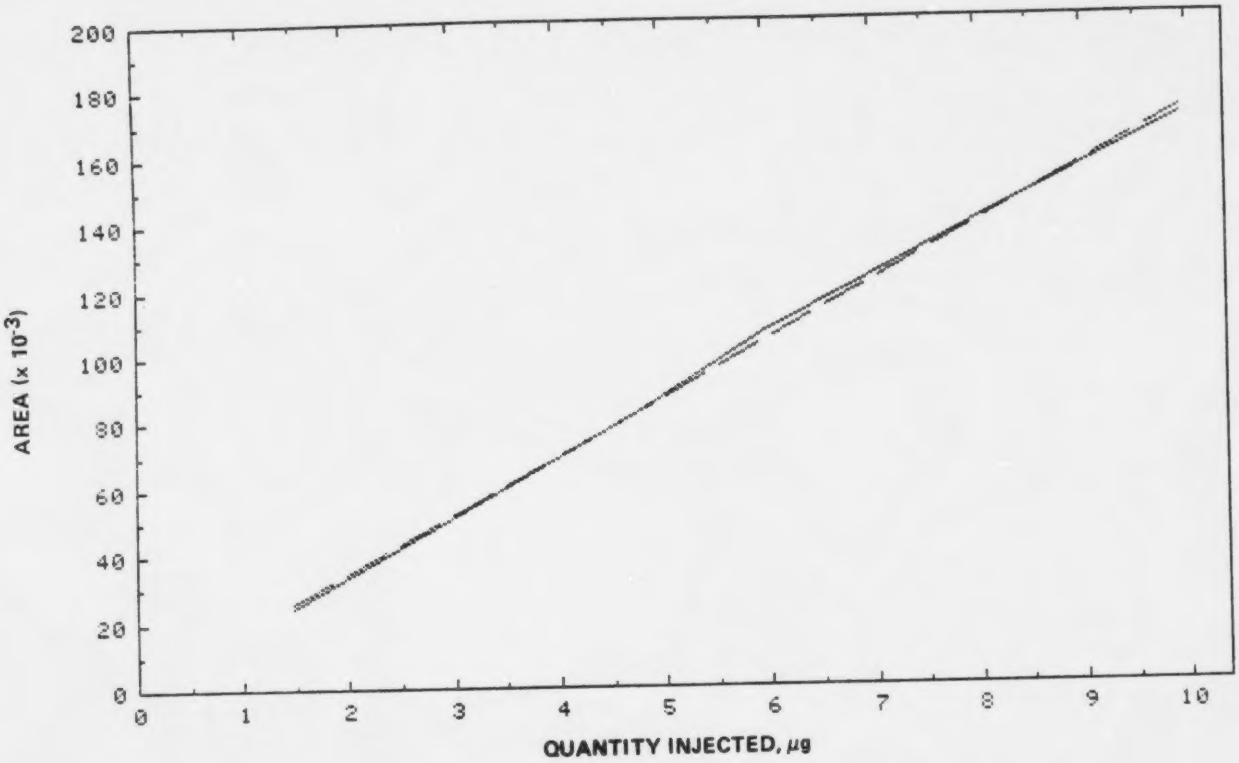

Figure C-56. Calibration curve for the determination of 2,4,5-trichlorophenoxyacetic acid by HPLC/UV.

Range: 1.5 - 9.9 µg
Correlation coefficient: 0.999
Slope: $1.7 \times 10^{+1}$
y-Intercept: -4.1×10^{-1}

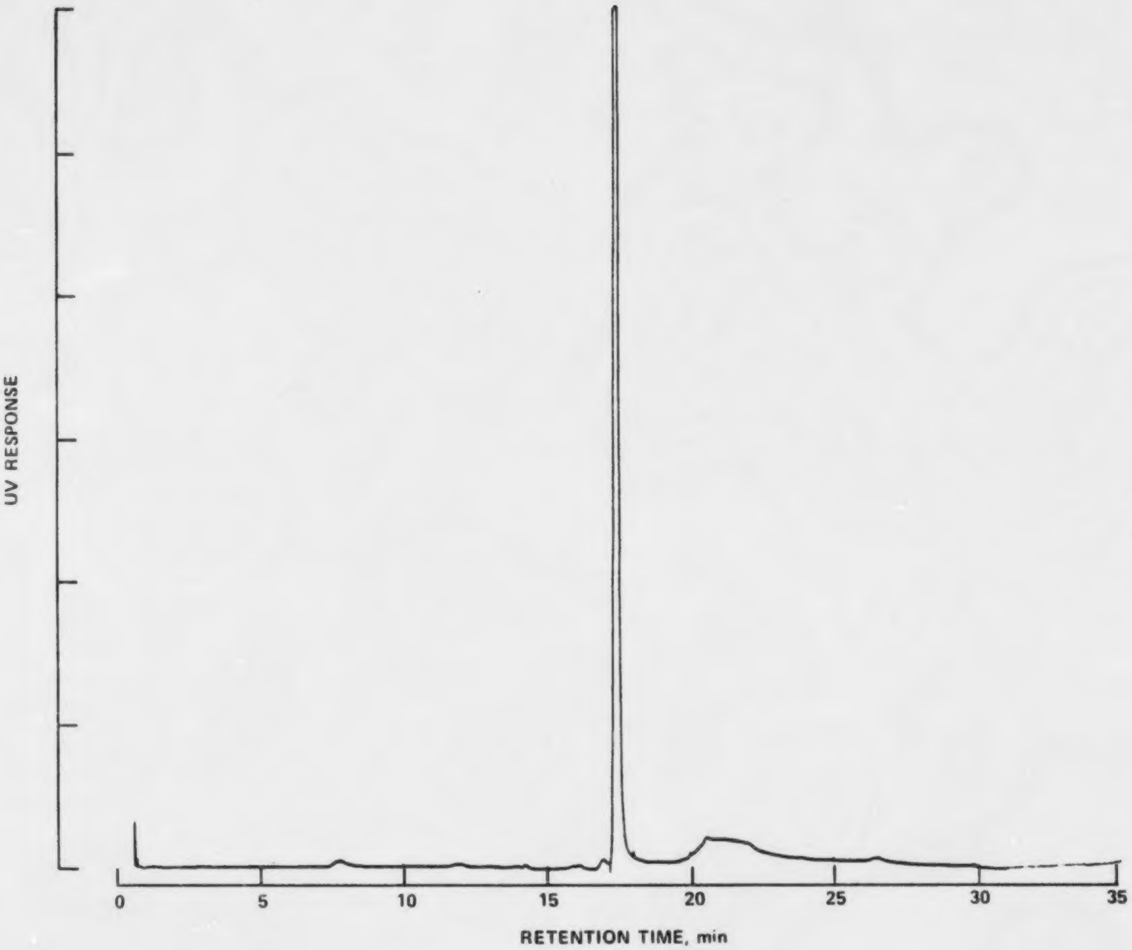

Figure C-57. Chromatogram by HPLC/UV for 2-(2,4,5-trichlorophenoxy)propionic acid.

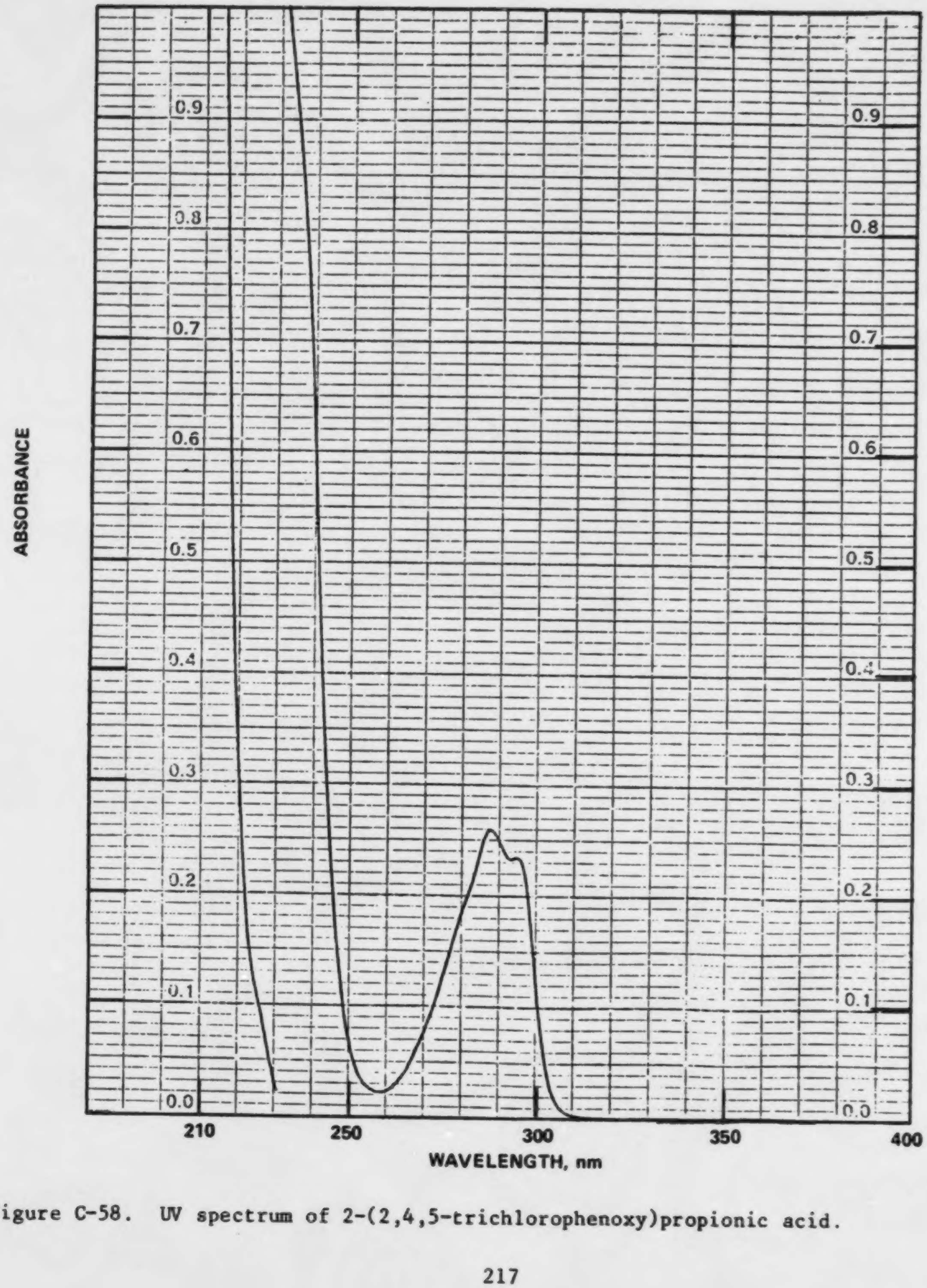

Figure C-58. UV spectrum of 2-(2,4,5-trichlorophenoxy)propionic acid.

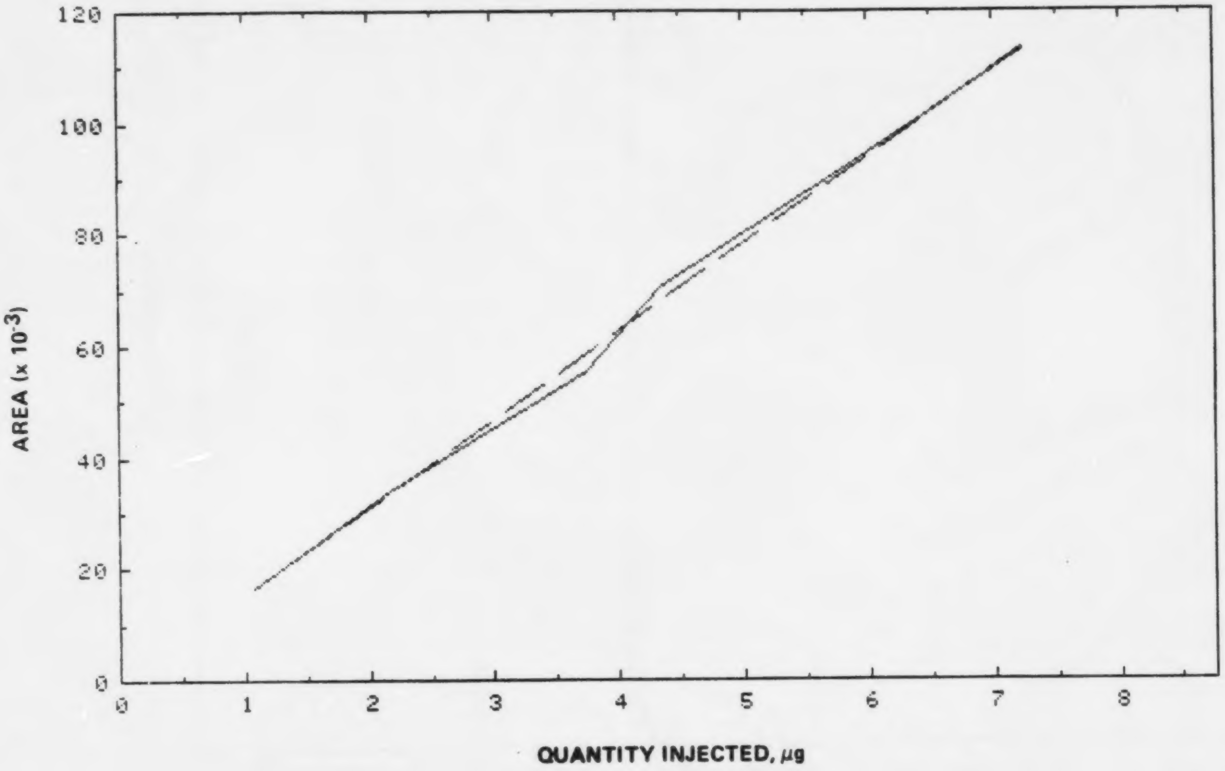

Figure C-59. Calibration curve for the determination of 2-(2,4,5-trichlorophenoxy)propionic acid by HPLC/UV.

Range: 1.1 - 7.2 µg
Correlation coefficient: 0.998
Slope: $1.6 \times 10^{+1}$
y-Intercept: -5.5×10^{-1}

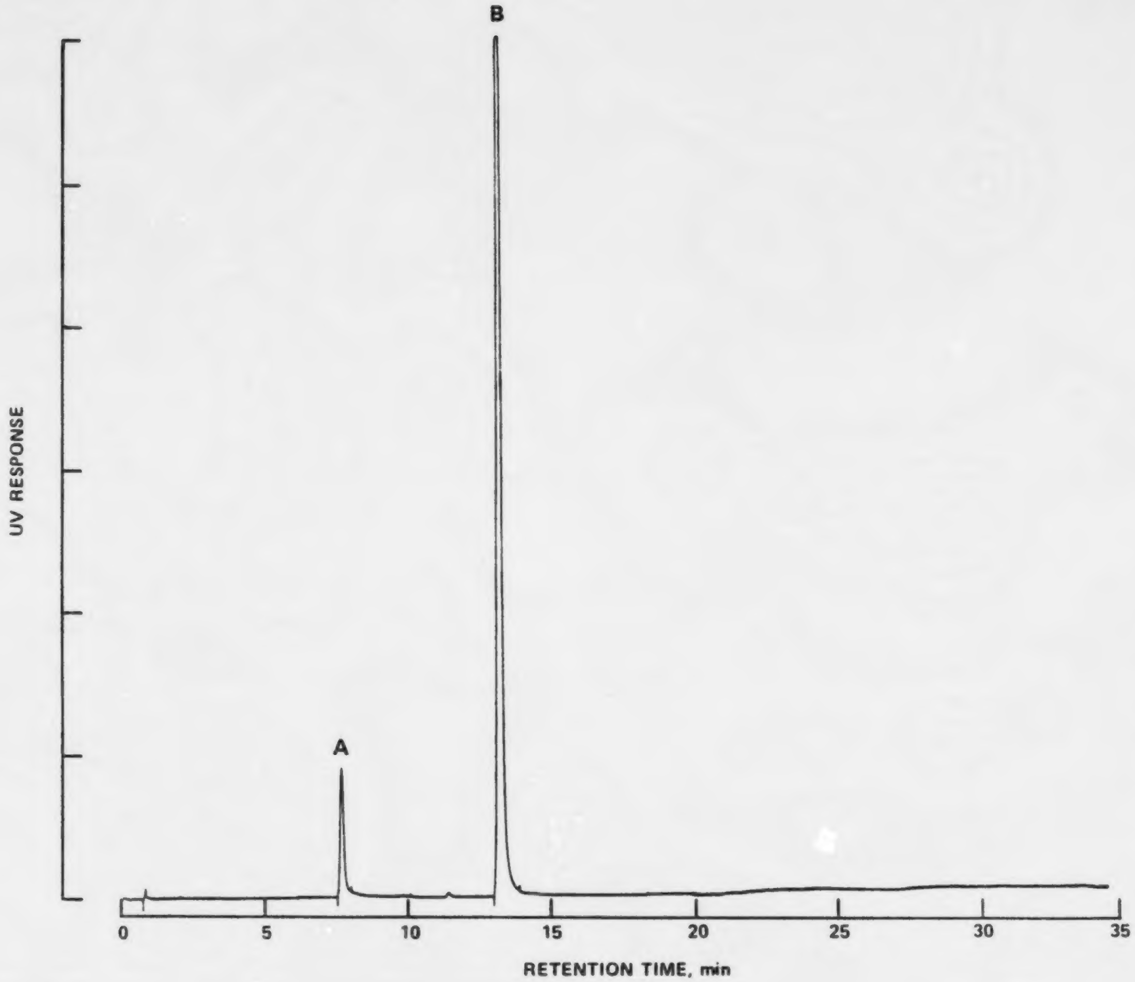

Figure C-60. Chromatogram by HPLC/UV for

(A) 4,6-dinitro-o-cresol(t_R = 7.5 min) and
(B) methyl yellow(t_R = 13.0 min).

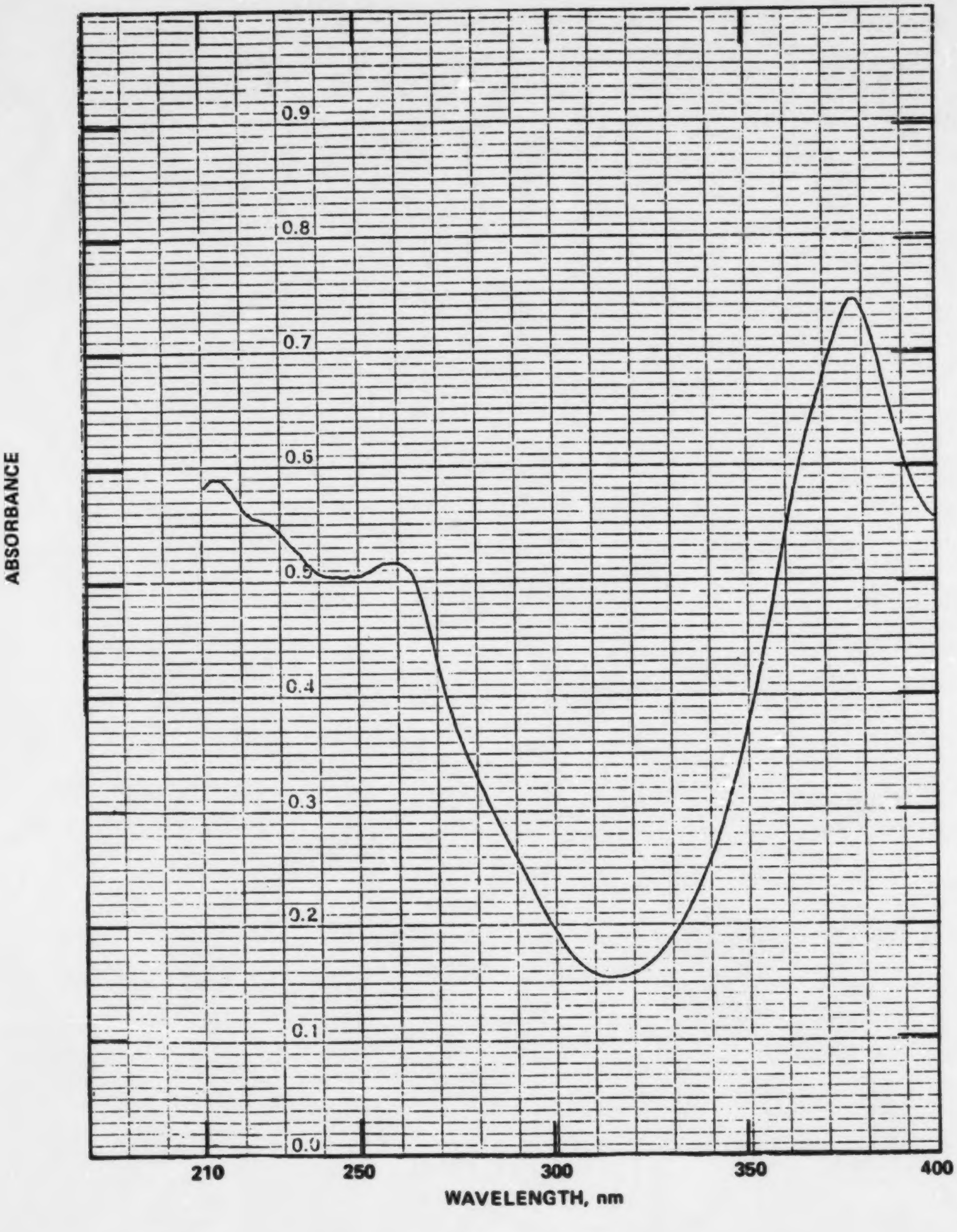

Figure C-61. UV spectrum of 4,6-dinitro-o-cresol.

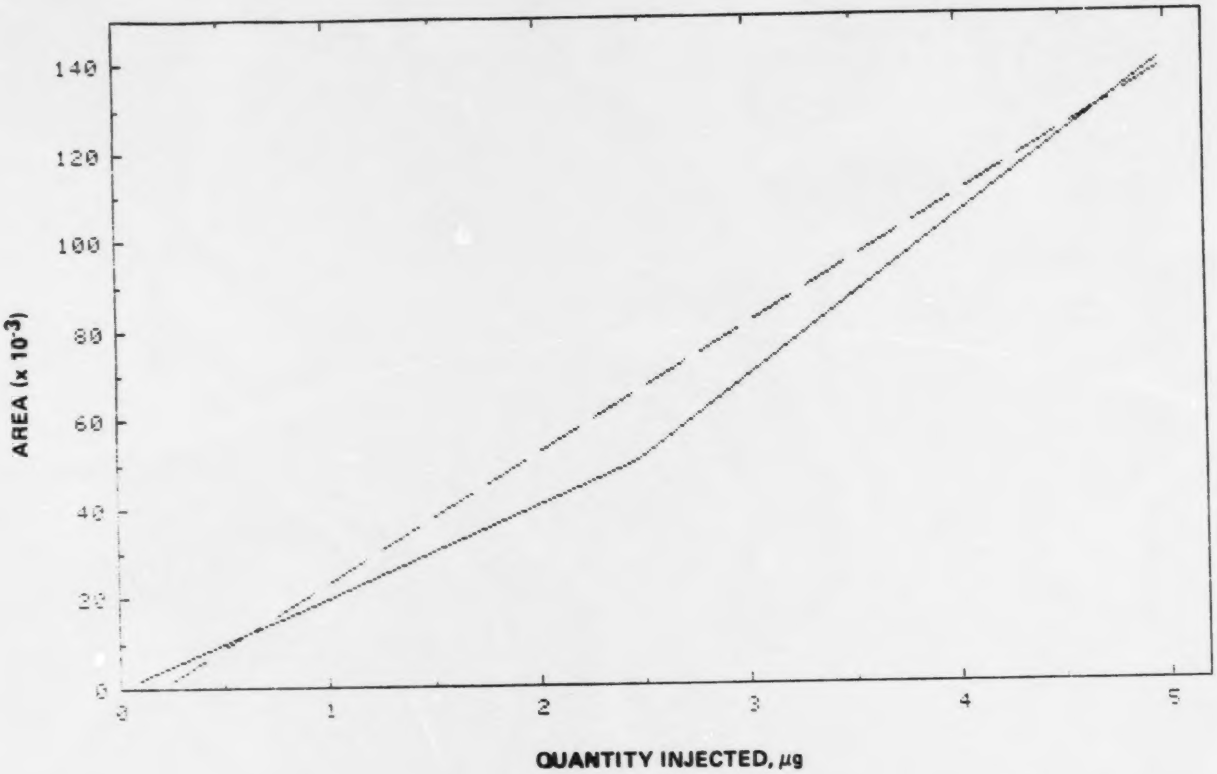

Figure C-62. Calibration curve for the determination of 4,6-dinitro-o-cresol by HPLC/UV(378nm).

Range: 0.50 - 5.0 µg
Correlation coefficient: 0.998
Slope: $2.9 \times 10^{+1}$
y-Intercept: -5.3

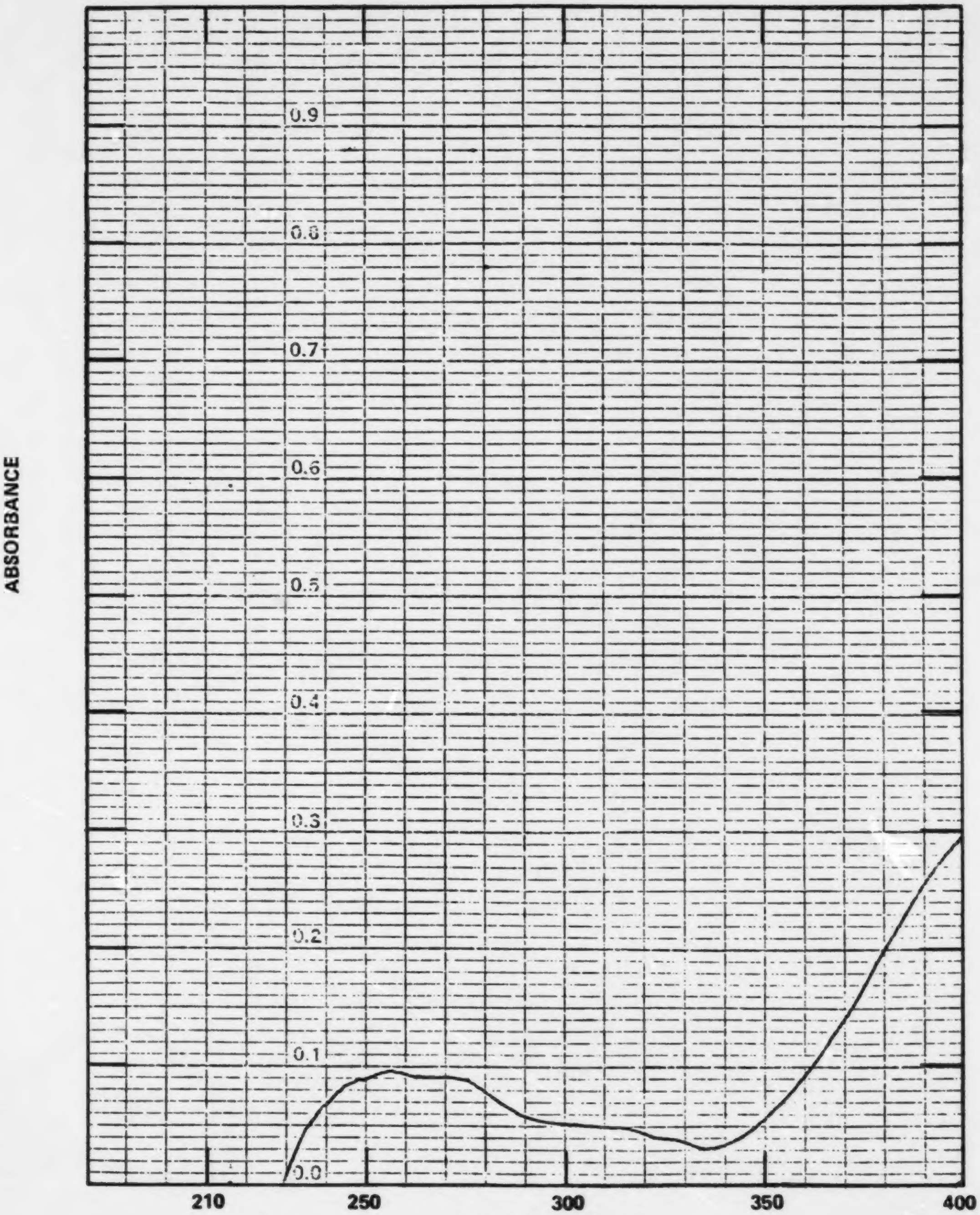

Figure C-63. UV spectrum of methyl yellow.

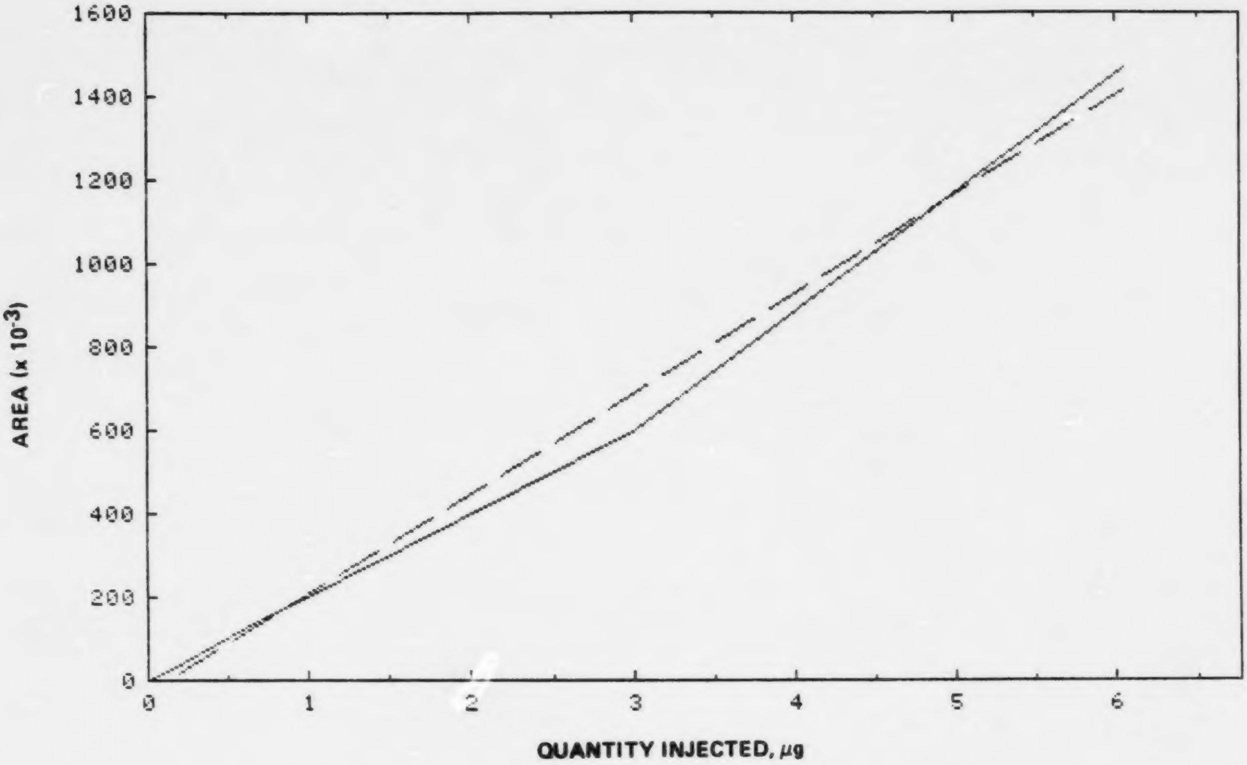

Figure C-64. Calibration curve for the determination of methyl yellow by HPLC/UV(400nm).

Range: 0.60 - 6.0 µg
Correlation coefficient: 0.995
Slope: $2.4 \times 10^{+2}$
y-Intercept: $-3.0 \times 10^{+1}$

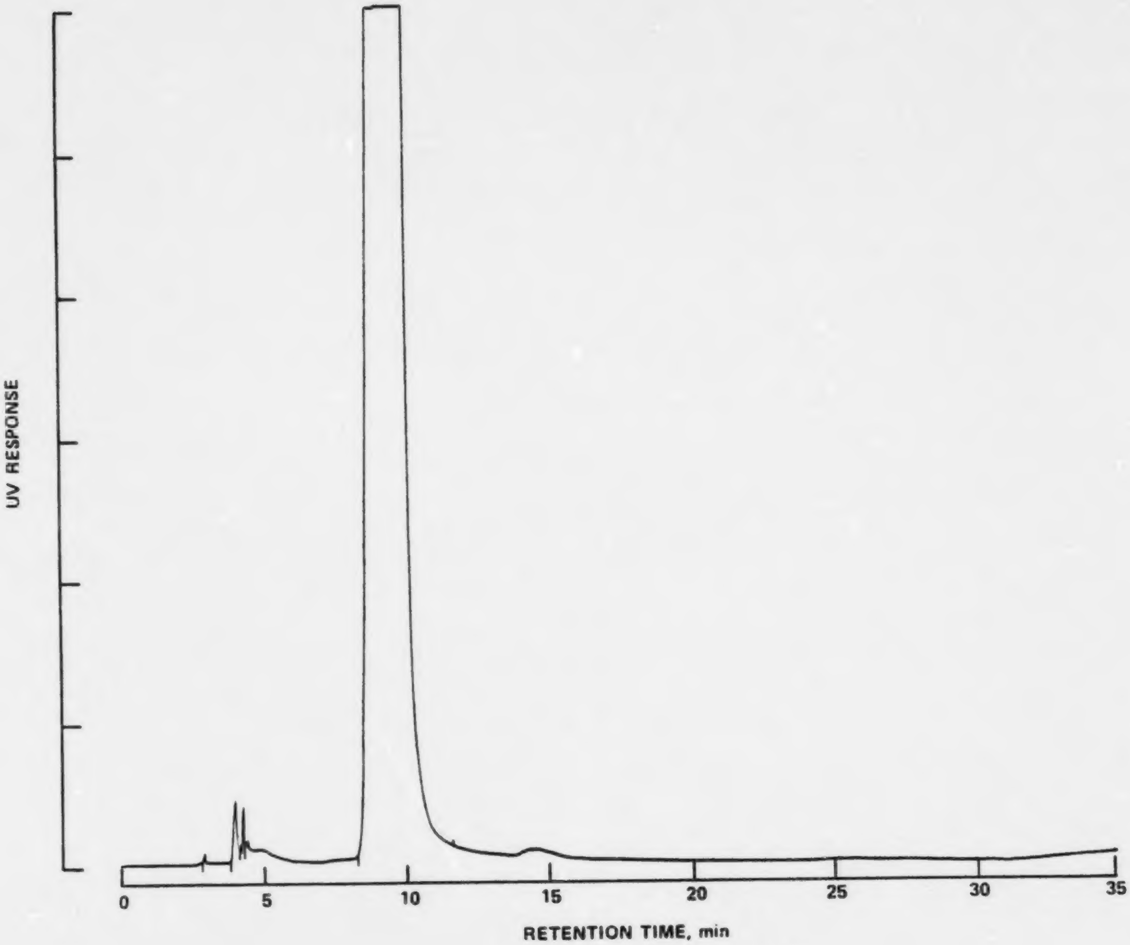

Figure C-65. Chromatogram by HPLC/UV for *N*-nitroso-*N*-methylurea.

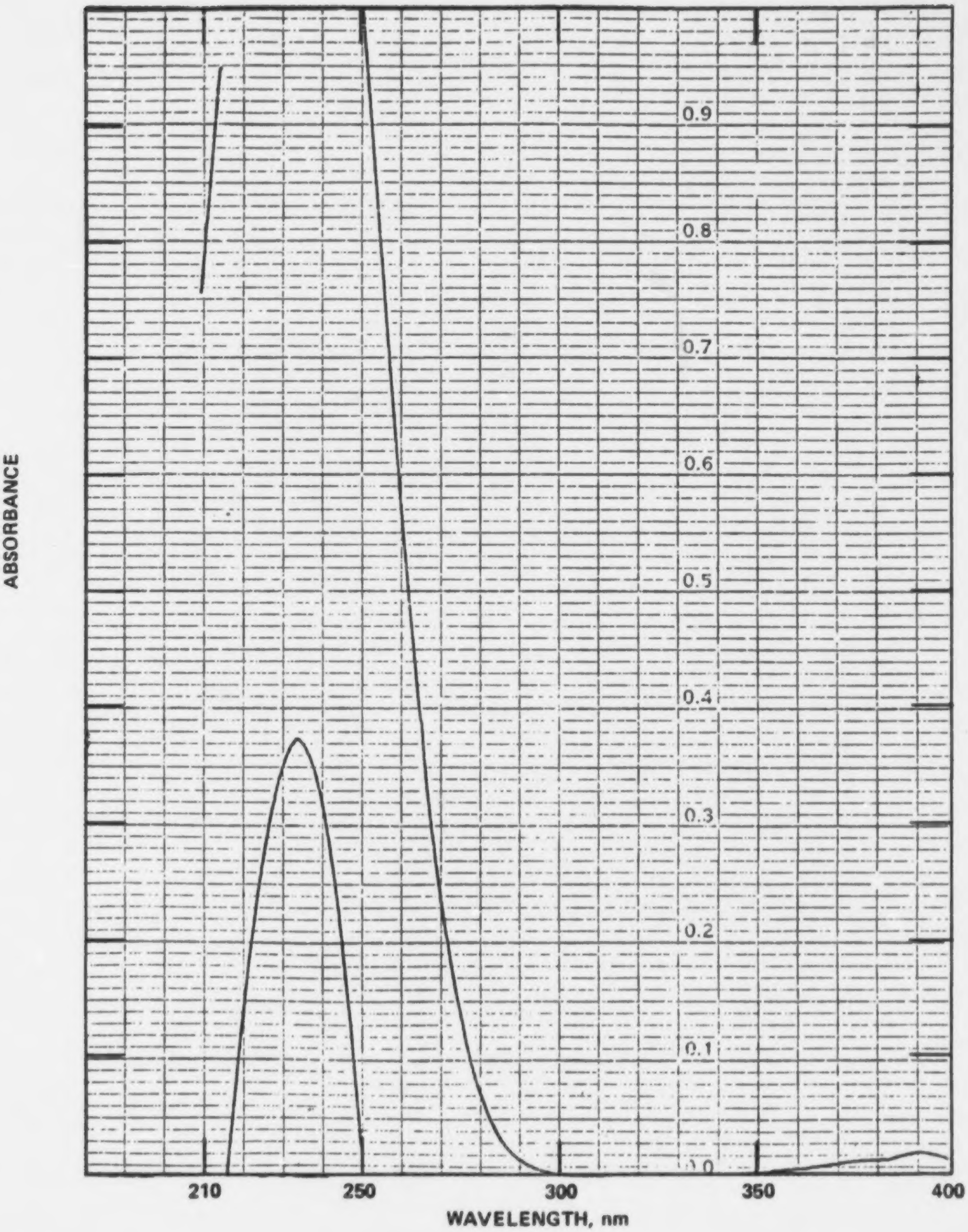

Figure C-66. UV spectrum of N-nitroso-N-methylurea.

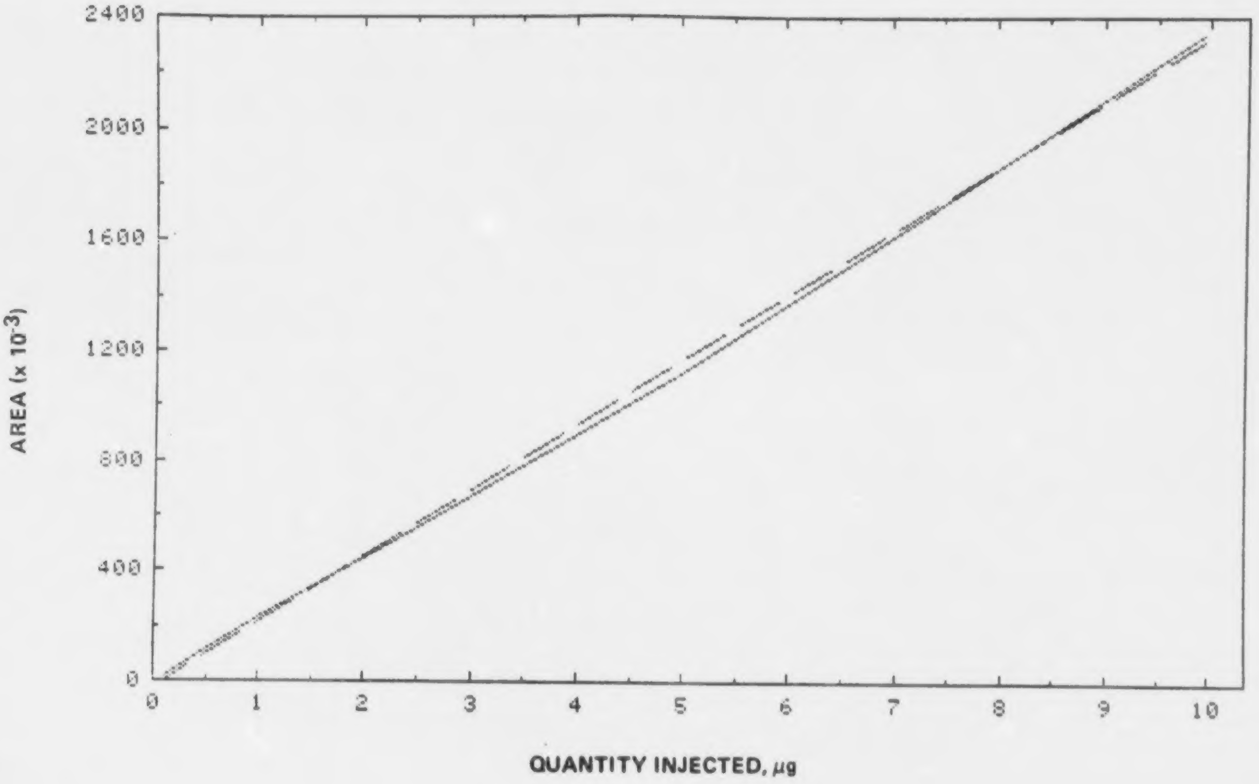

Figure C-67. Calibration curve for the determination of N-nitroso-N-methylurea by HPLC/UV.

Range: 0.50 - 9.9 μg
Correlation coefficient: 0.999
Slope: $2.4 \times 10^{+2}$
y-Intercept: $-2.0 \times 10^{+1}$

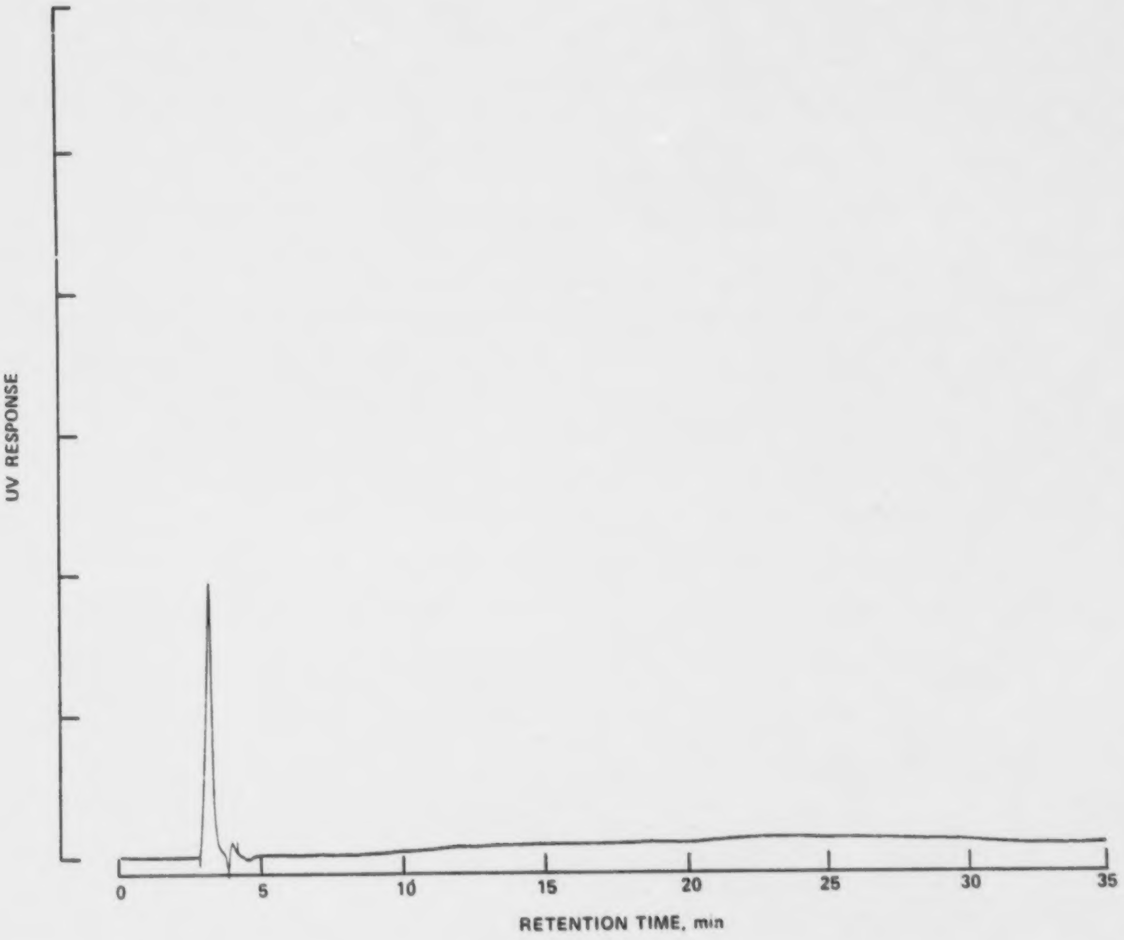

Figure C-68. Chromatogram by HPLC/UV for saccharin.

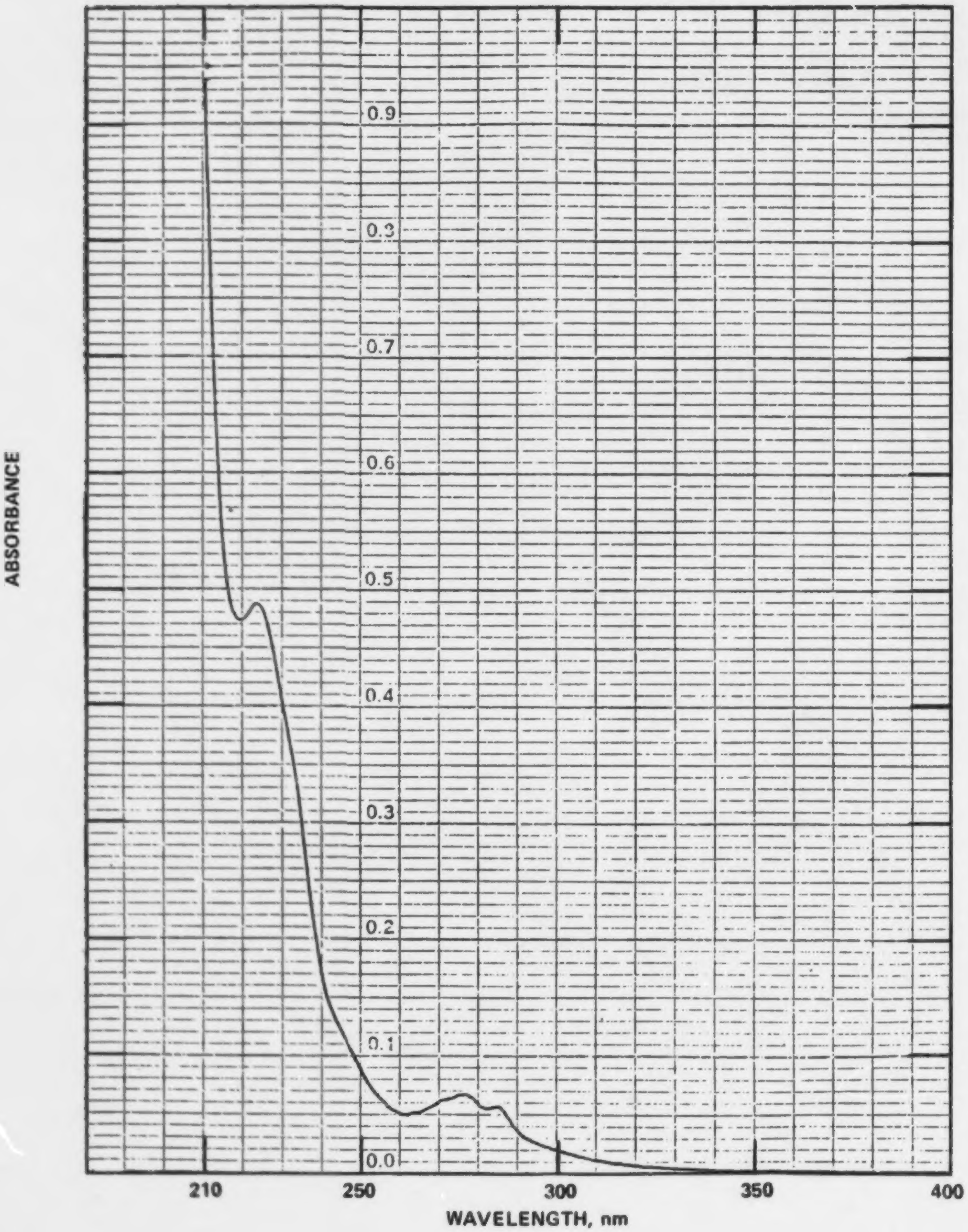

Figure C-69. UV spectrum of saccharin.

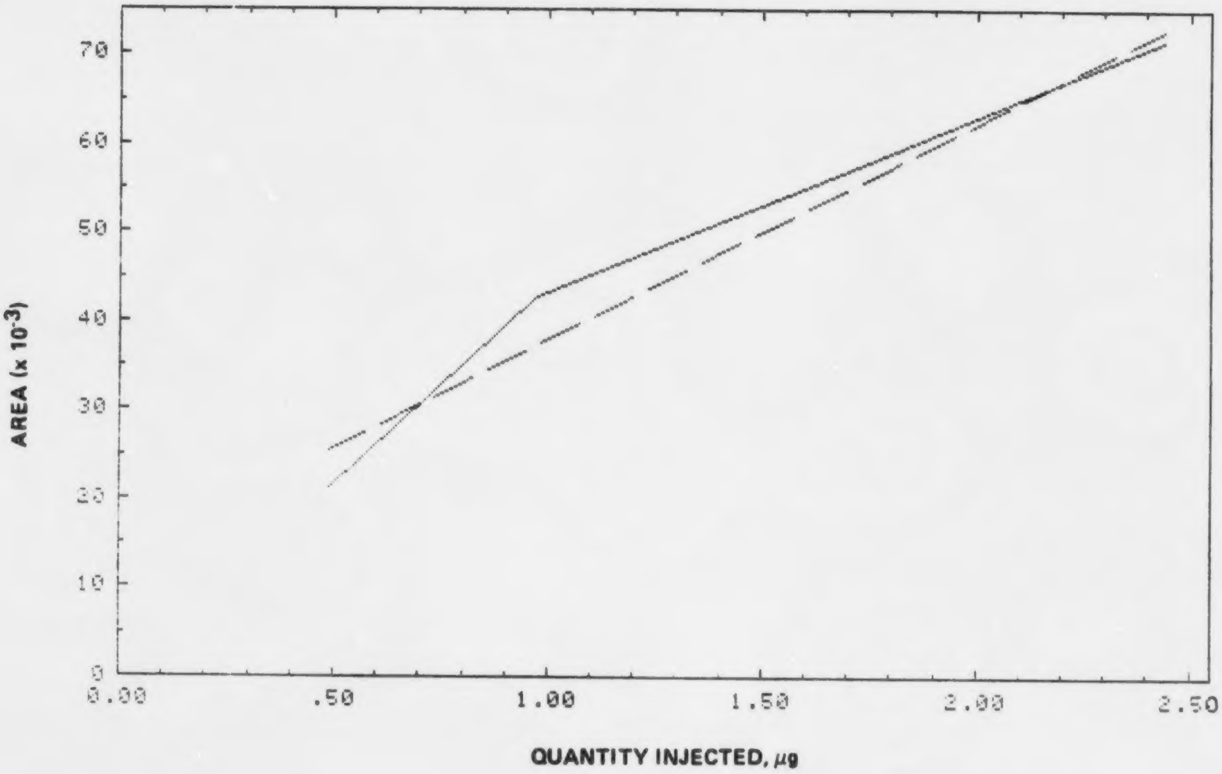

Figure C-70. Calibration curve for the determination of saccharin by HPLC/UV.

Range: 0.49 - 2.4 μg
Correlation coefficient: 0.980
Slope: $2.4 \times 10^{+1}$
y-Intercept: $1.4 \times 10^{+1}$

APPENDIX D

DESCRIPTION OF SUPPLEMENTARY METHOD DEVELOPMENT AND OTHER TASKS

INTRODUCTION

Battelle-Columbus Laboratories, Columbus, Ohio, in a joint effort with Southern Research Institute, undertook specific tasks to supplement the development of generalized test procedures. Specific analysis methods for brucine and 2-fluoroacetamide were developed. Also, potentially useful air-sampling, sample-preparation, and analysis procedures for various POHCs were recommended. Existing preparative and analysis methods for the determination of metals in wastes and incinerator effluents were refined and supplemented. These tasks are reported in the following sections of this appendix.

DEVELOPMENT OF ANALYSIS METHODS FOR BRUCINE AND 2-FLUOROACETAMIDE

Because spectrophotometric analysis methods are given in the Methods Manual for these two compounds, gas chromatographic analysis procedures were sought for their determination. The developed generalized GC procedures described previously, however, were not entirely suitable for these two compounds. Consequently, GC conditions were modified to accommodate the determination of the compounds. The conditions found optimum for brucine are given on page 231. Under the specified conditions, the detection limit was estimated to be between 5 and 20 ng in a single injection. A chromatogram of brucine is presented as Figure D-1.

The optimum conditions found for the determination of 2-fluoroacetamide are given on page 233. The detection limit was about 20 ng of 2-fluoroacetamide in a single injection. A chromatogram of the compound is presented as Figure D-2.

Method Number:

Method Name: Brucine[*]

Basic Method: GC/FID

Matrix: Organic solvent extract of waste sample or sampling medium

Specific POHC from Appendix VIII to which method may be applied: Brucine

Apparatus: GC/FID

Analysis-Method Parameters:

GC:
- Column -- Fused-silica capillary, 30 m long, 0.25-mm ID, wall-coated with SE-52
- Carrier gas -- He at 2 mL/min
- Temperature program -- 120 to 300 °C at 8 °C/min; 300 °C, 32 min isothermal
- Injector temperature -- 300 °C

FID:
- Detector temperature -- 300 °C
- Detection limit -- 5 to 20 ng

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[*] This method was developed by Battelle-Columbus Laboratories, Columbus, Ohio.

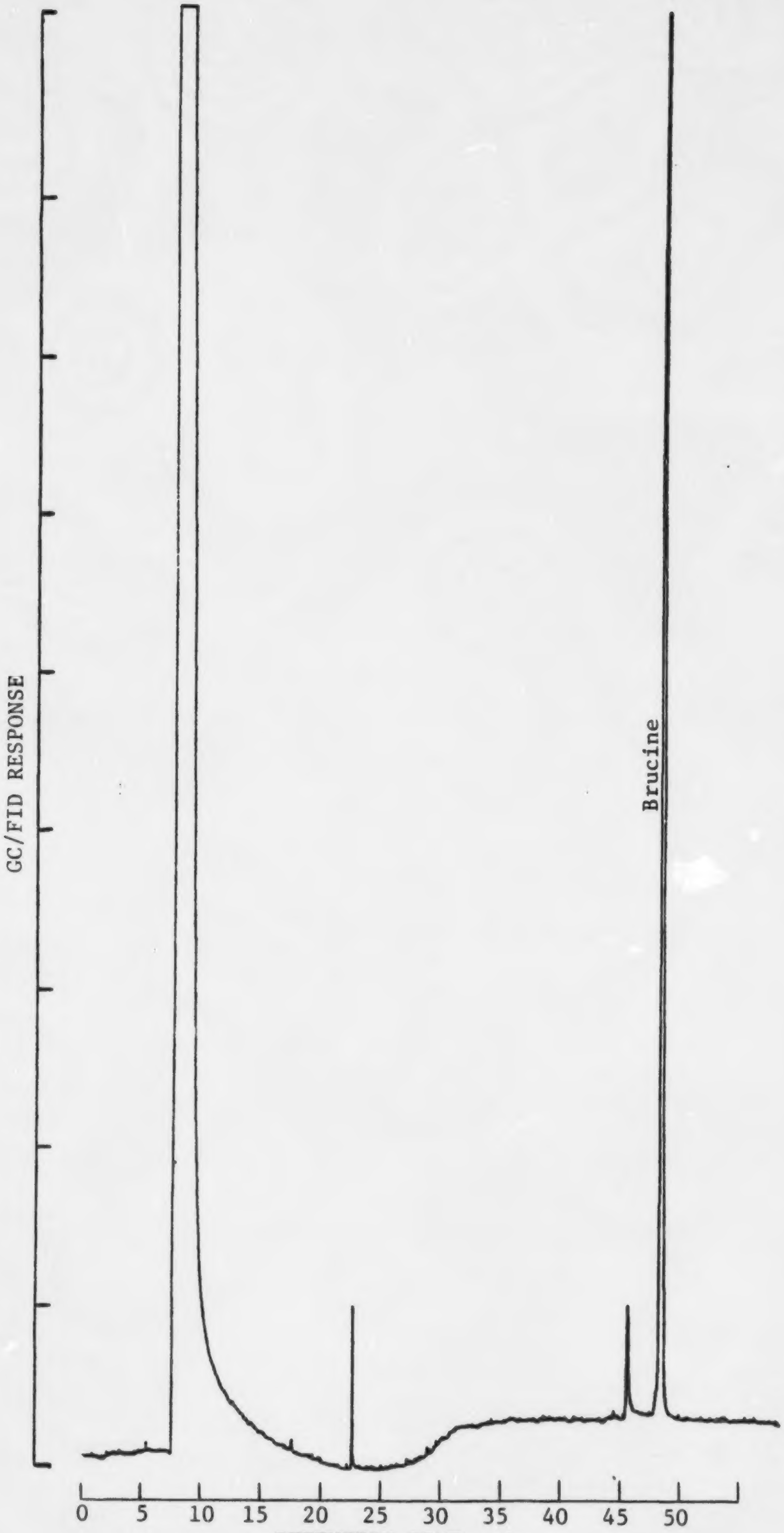

Figure D-1. Chromatogram by GC/FID for brucine (200 ng).

Method Number:

Method Name: 2-Fluoroacetamide*

Basic Method: GC/FID

Matrix: Organic solvent extract of waste sample or sampling medium

Specific POHC from Appendix VIII to which method may be applied: 2-Fluoroacetamide

Apparatus: GC/FID

Analysis-Method Parameters:

GC:
Column -- Chromosorb 101 (100/120 mesh), 1.8 m x 2-mm ID
Carrier gas -- He at 30 mL/min
Temperature program -- 155 °C isothermal

FID:
Detector temperature --
Detection limit -- ≈20 ng

References:

1. Warner, J. S., and M. C. Landes, Internal Communication, Battelle-Columbus Laboratories, November 10, 1981.

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*This method was developed by Battelle-Columbus Laboratories, Columbus, Ohio.

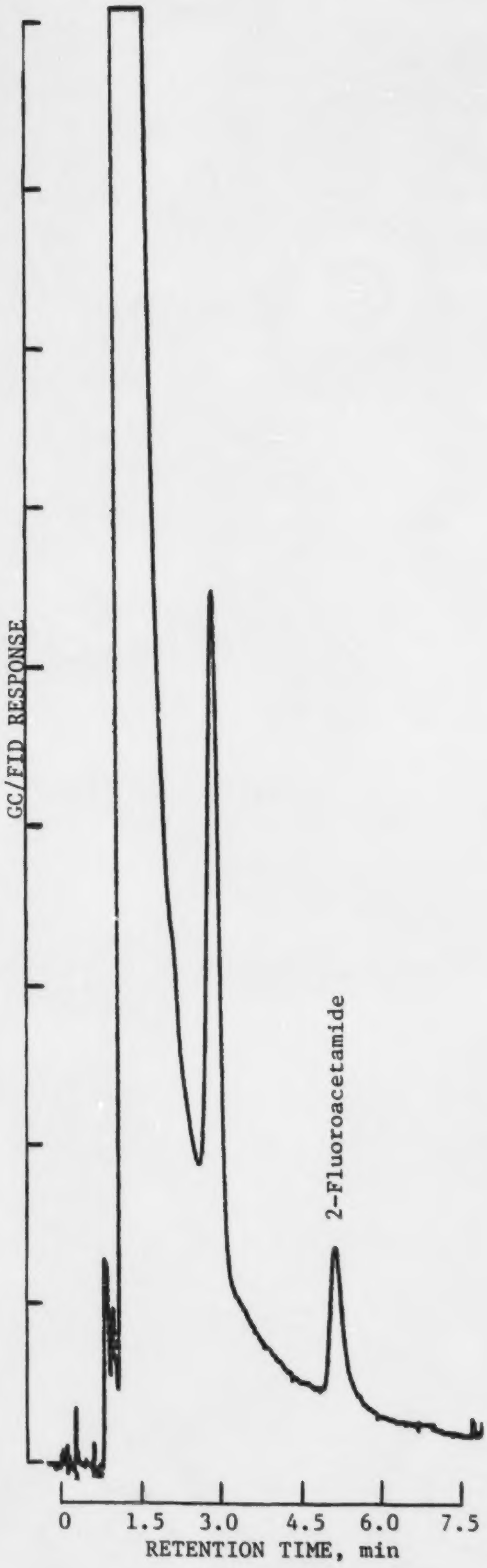


Figure D-2. Chromatogram by GC/FID for 2-fluoroacetamide (100 ng).

RECOMMENDATION OF POTENTIALLY USEFUL AIR-SAMPLING, SAMPLE-PREPARATION, AND ANALYSIS PROCEDURES FOR VARIOUS POHCs

As part of the work performed in the initial phase of this contract assignment, overall air-sampling and analysis methods were proposed for the determination of particular chemical classes of POHCs. On the basis of professional judgment and information found in literature references, these methods were suggested as refinements of and additions to the methods already given in the Methods Manual.

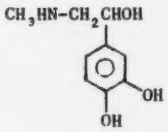
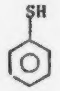
The classes of compounds that were considered included those listed in Table C.4 of the Methods Manual--aldehydes, acids, and esters--and those listed in Table C.4--alcohols and thiols. The specific compounds given consideration are listed in Table D-1 of this appendix along with their corresponding Chemical Abstracts Service (CAS) Registry numbers, chemical structures and formulas, molecular weights, boiling points (or flash points or melting points), and brief summary statements describing the proposed air-sampling, sample-preparation, and analysis procedures. The compounds in Table D-1 have been separated into groups according to the following scheme:

Group notation	Chemical class or chemical name
C-5-B	Alcohols
C-5-C	Epinephrine
C-5-A	Thiols
C-4-C	Aldehydes
C-4-B	Organophosphorus compounds
C-4-E	Organosulfur compounds
C-4-F	Trifluoroacetic acid, sodium salt
C-4-D	Methyl methacrylate
C-4-A	Carboxylic acids

The air-sampling methods given in Table D-1 require the use of two sampling trains. For the collection of most of the compounds, a modified version of the EPA Method 5 train is appropriate. This modified train was developed by Battelle-Columbus Laboratories; a diagram of its components is given as Figure D-3. Another sampling train was recommended for the collection of aldehydes in air; this device is presented in Figure D-4. The collection media for aldehydes is sodium bisulfite in aqueous solution. The collected aldehyde is then derivatized with dinitrophenylhydrazine or 2,3,4,5,6-pentafluorobenzylhydrazine for determination by GC.

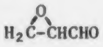
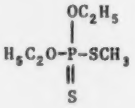
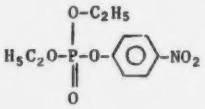
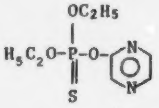
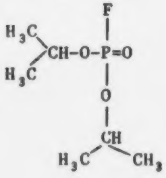
Detailed descriptions of the proposed methods for each group of compounds shown in Table D-1 are presented on pages 243 through 281.

TABLE D-1. PROPOSED AIR SAMPLING AND ANALYSIS METHODS FOR SELECTED POHCs

CAS Registry No.	Name	Structure	Formula	Mol wt	bp, °C[a]		Air sampling and sample preparation methods	Analysis method
107-18-6	(Allyl alcohol) 2-Propen-1-ol	$CH_2=CH-CH_2-OH$	C_3H_6O	58	96-98	C-5-B	Modified Method 5 (MM5) (extraction with water of sorbent and filter)	GC/FID (glass column packed with 0.8% THEED[b] on Carbopak) or GC/MS (capillary glass column wall-coated with SE-52)
107-19-7	2-Propyn-1-ol	$HC\equiv C-CH_2-OH$	C_3H_4O	56	114-115			
57-55-6	1,2-Propanediol	$CH_3-CHOH-CH_2OH$	$C_3H_8O_2$	76	187			
51-43-4	Epinephrine	CH_3HN-CH_2CHOH 	$C_9H_{13}O_3N$	183	mp 211-212	C-5-C	Modified Method 5 (MM5) (extraction with 1% HCl of sorbent (alumina) and filter)	LCEC[c] or GC/MS (capillary glass column wall-coated with SE-52)
108-98-5	Benzenethiol		C_6H_5SH	110	168-169	C-5-A	Modified Method 5 (MM5) (extraction with methylene chloride of XAD-2 sorbent and filter)	GC/ECD[d] or GC/MS (glass capillary column wall-coated with SE-52)
594-42-3	Tetrachloromethanethiol	CCl_3SCl	CCl_4S	186	147-148			
75-70-7	Trichloromethanethiol	CCl_3SH	$CHCl_3S$	152	—			

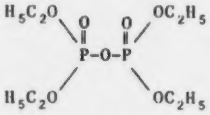
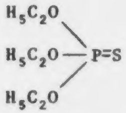
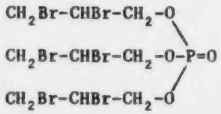
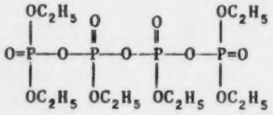
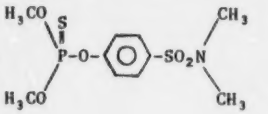
(continued)

TABLE D-1 (continued)

CAS Registry No.	Name	Structure	Formula	Mol wt	bp, °C[a]	Air sampling and sample preparation methods	Analysis method
75-07-0	Acetaldehyde	CH_3CHO	C_2H_4O	44	21	C-4-C Modified Method 5 (MM5) (impinger with derivatizing agent such as DNPH[f])	GC/ECD[e] or MS (glass capillary column wall-coated with SE-52) or HPLC (Zorbax-ODS, 75% methanol/25% H_2O)
4170-30-3	Crotonaldehyde	$CH_3CH{=}CHCHO$	C_4H_6O	70	104		
765-34-4	Glycidylaldehyde	 $H_2C(O)C{-}CHCHO$	$C_3H_4O_2$	72	112-113		
107-20-0	Chloroacetaldehyde	$CH_2Cl{-}CHO$	C_2H_3OCl	78	85-86		
3288-58-2	O,O-Diethyl-S-methyl-ester phosphorodithioic acid		$C_5H_{13}O_2S_2P$	200	—	C-4-B Modified Method 5 (MM5) (XAD-2 sorbent, extraction with methylene chloride)	GC/AFID[g] or GC/MS (glass capillary wall-coated with SE-52 column)
311-45-5	O-p-Nitrophenyl ester, O,O-diethyl phosphoric acid		$C_{10}H_{14}NO_6P$	275	—		
297-97-2	O,O-Diethyl-O-(2-pyrazinyl) phosphorothioate		$C_8H_{13}N_2O_3PS$	217	—		
55-91-4	Diisopropyl fluorophosphate		$C_6H_{14}FO_3P$	184	62 (9 torr)		

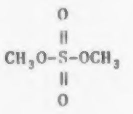
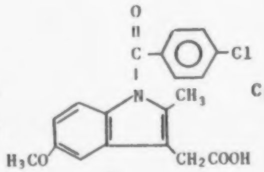
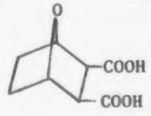
(continued)

TABLE D-1 (continued)

CAS Registry No.	Name	Structure	Formula	Mol wt	bp, °C[a]	Air sampling and sample preparation methods	Analysis method
3689-24-5	Tetraethyldithiopyrophosphate	$(C_2H_5O)_2P(S)OP(S)(OC_2H_5)_2$	$C_8H_{20}O_5P_2S_2$	322	136-139	C-4-B (continued) Modified Method 5 (MM5) (XAD-2 sorbent, extraction with methylene chloride)	GC/AFID or GC/MS (glass capillary column wall-coated with SE-52)
107-49-03	Tetraethyl pyrophosphate		$C_3H_{20}O_7P_2$	290	13		
126-68-1	O,O,O-Triethylphosphorothioate		$C_6H_{15}O_3PS$	198	100 (16 torr)		
126-72-7	Tris(2,3-dibromopropyl) phosphate		$C_9H_{15}Br_6O_4P$	218	fp >112		
757-58-4	Hexaethyl tetraphosphate		$C_{12}H_{30}O_{13}P_4$	506	decomposes above 150 °C		
52-85-7	Phosphorothioic acid-O,O-dimethyl ester, O-ester with sulfonamide benzene		$C_{10}H_{16}O_5NS_2$	325	mp 52-53		

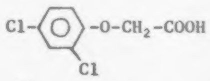
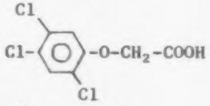
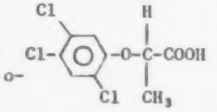
(continued)

TABLE D-1 (continued)

CAS Registry No.	Name	Structure	Formula	Mol wt	bp, °C[a]	Air sampling and sample preparation methods	Analysis method
77-78-1	Dimethyl sulfate	 $CH_3O\text{-}\overset{O}{\underset{O}{\overset{\parallel}{\underset{\parallel}{S}}}}\text{-}OCH_3$	$C_2H_6O_4Cl$	126	188 (with decomposition)	C-4-E Modified Method 5 (MM5) (XAD-2 or Porapak Q or silica gel sorbent and acetone or water extraction)	GC/MS (glass capillary column wall-coated with SE-52)
62-50-0	Ethylmethane sulfonate	$CH_3SO_3C_2H_5$	$C_3H_8O_3S$	124	—		
66-27-3	Methyl methane sulfonate	$CH_3SO_3CH_3$	$C_2H_6O_3S$	110	—		
62-74-8	Trifluoroacetic acid, Na salt	$CF_3COO^-Na^+$	$C_2O_2F_3Na$	136	—	C-4-D Modified Method 5 (MM5) (filter and impinger [10% HNO_3] and steam distillation)	GC/ECD or MS (glass capillary column wall-coated with SE-52)
80-52-6	Methyl methacrylate	$CH_2C(CH_3)COOCH_3$	$C_5H_8O_2$	100	101	C-4-D Modified Method 5 (MM5) (XAD-2 sorbent, extraction with methylene chloride)	GC/FID or MS (glass capillary column wall-coated with SE-52)
53-86-1	1-(p-Chlorobenzoyl)-5-methoxy-2-methylindole-3-acetic acid		$C_{15}H_{16}O_4NCl$	357	mp 155	C-4-A Modified Method 5 (MM5) (particulate and filter, then diethyl ether extraction)	Derivatization (diazomethane), GC/ECD or MS (glass capillary [SE-52] or packed [OV-1 on Gas-Chrom Q] column)
145-73-3	7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid		$C_8H_{10}O_5$	180	—		

(continued)

TABLE D-1 (continued)

CAS Registry No.	Name	Structure	Formula	Mol wt	bp, °C[a]	Air sampling and sample preparation methods	Analysis method
94-75-7	2,4-dichlorophenoxyacetic acid		$C_8H_6O_3Cl_2$	221	—	C-4-A (continued)	
93-76-5	2,4,5-trichlorophenoxyacetic acid		$C_8H_5Cl_3O_3$	255	mp 151-153	Modified Method 5 (MM5) (particulate and filter, then diethyl ether extraction)	Derivatization (diazomethane), GC/ECD or MS (glass capillary [SE-52] or packed [OV-1 on Gas-Chrom Q] column)
93-72-1	2-(2,4,5-trichlorophenoxy)propionic acid o-		$C_9H_7Cl_3O_3$	270	mp 180-181		

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[a] Boiling points (bp) are given except when flash points (fp) and melting points (mp) are indicated.

[b] THEED = tetrahydroxyethylene amine.

[c] LCEC = liquid chromatography with electrochemical detection.

[d] GC/FPD = gas chromatography with flame photometric detection.

[e] GC/ECD = gas chromatography with electron capture detection.

[f] DNPH = 2,4-dinitrophenylhydrazine.

[g] GC/AFID = gas chromatography with alkali flame ionization detection.

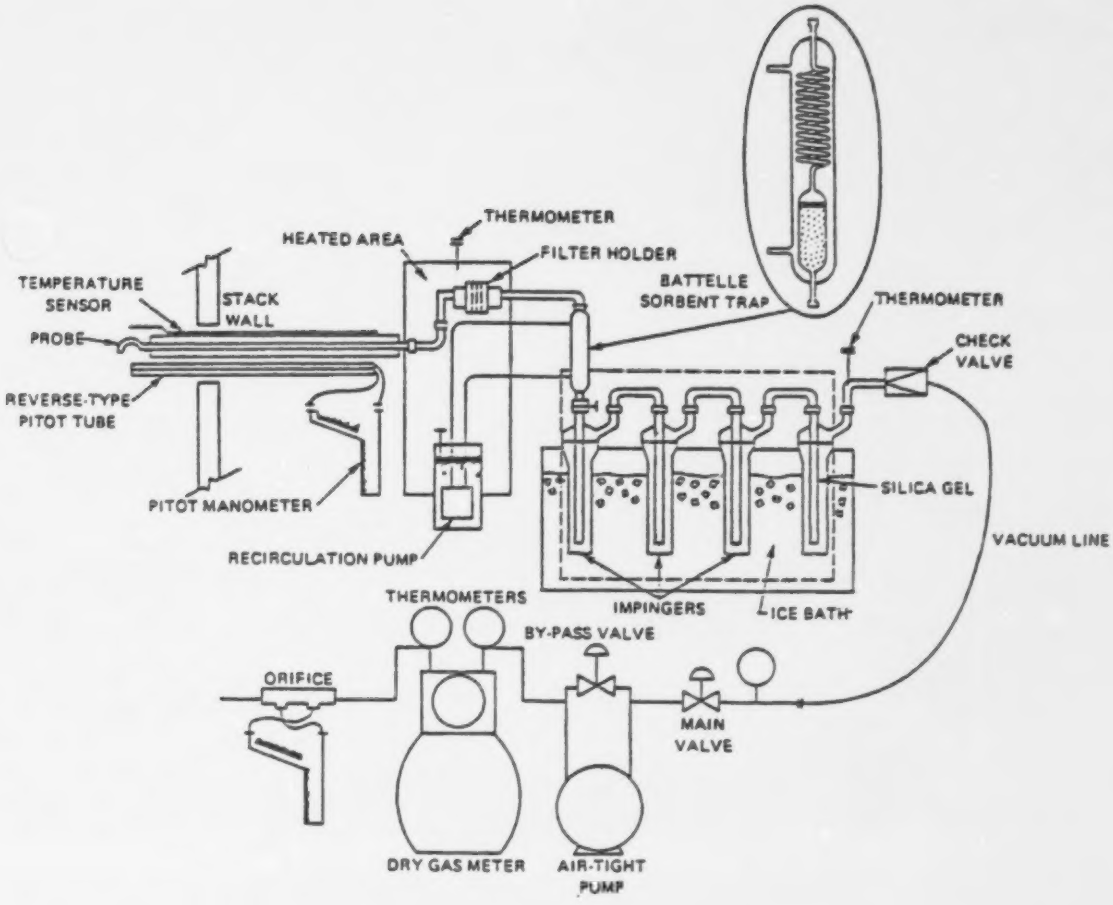
THERMOMETER
HEATED AREA
FILTER HOLDER
TEMPERATURE SENSOR
STACK WALL
BATTELLE SORBENT TRAP
THERMOMETER
PROBE
CHECK VALVE
REVERSE-TYPE PITOT TUBE
SILICA GEL
PITOT MANOMETER
VACUUM LINE
RECIRCULATION PUMP
THERMOMETERS
IMPINGERS
ICE BATH
BY-PASS VALVE
ORIFICE
MAIN VALVE
DRY GAS METER
AIR-TIGHT PUMP

Figure D-3. Battelle Modified Method (MM5) Train.

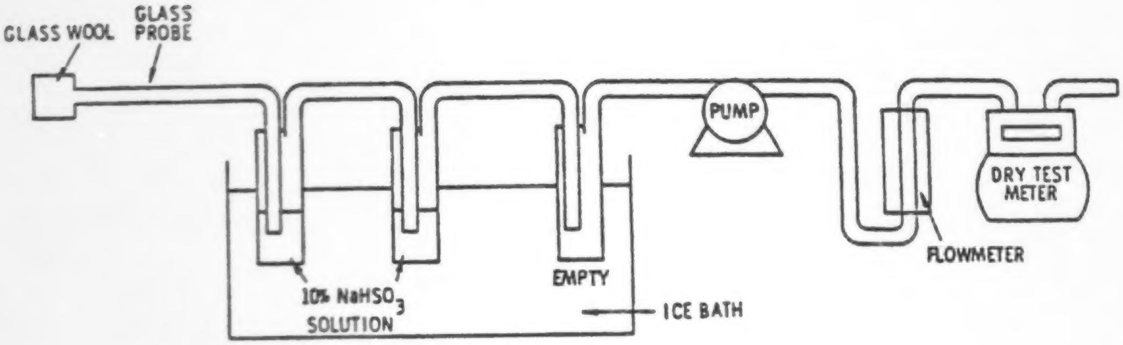
GLASS WOOL
GLASS PROBE
PUMP
DRY TEST METER
FLOWMETER
EMPTY
10% NaHSO3 SOLUTION
ICE BATH

Figure D-4. Diagram of sampling train for aldehydes.

EXAMPLE 1. POHC SAMPLING METHOD

Method Number:

Method Name: Modified Method 5 (MM5)

Basic Method: Comprehensive sampling train (filter-sorbent-impinger)

Matrix: Stack gas (particulate plus vapor-phase material)

Specific POHC from Appendix VIII to which method may be applied: Alcohols (Allyl alcohol, 2-Propyn-1-ol, 1,2-Propanediol) (C-5-B)

Apparatus: GC/FID

Sampling-Method Parameters:

Hardware: RAC or equivalent sampling train modified to include sorbent module as shown in Figure 3
Filter -- Glass-fiber filter
Sorbent -- XAD-2 resin
Impinger reagent -- Water

Deployment: Traverse and sample isokinetically as specified in EPA Method 1-5
Collect 5-m^3 sample at approximately 0.75-ft^3/min sampling rate

Recovery Check: Spike filter/sorbent or impingers before (or both) sampling with known quantity of deuterated or fluorinated analog of target compound.

References:

EXAMPLE 1: POHC SAMPLE-PREPARATION METHOD

Method Number:

Method Name: Extraction

Basic Method: 20-min shaking of filter and XAD-2 sorbent in water

Matrix:
Sorbent and solid waste and filter
Liquid waste (organic)

Specific POHC from Appendix VIII to which method may be applied: Alcohols (Allyl alcohol, 2-Propyn-1-ol, 1,2-Propanediol) (C-5-B)

Extraction-Method Parameters:
Apparatus -- Standard Equipment
Solvent -- Water
Time -- 20 min
Sample size -- 20-200 g

EXAMPLE 1. POHC ANALYSIS METHOD

Method Number:	
Method Name:	Alcohols
Basic Method:	GC/FID, GC/MS
Matrix:	Water (impinger and extract) Liquid organic waste (neat and dilute)
Specific POHC from Appendix VIII to which method may be applied:	Alcohols (Allyl alcohol, 2-Propyn-1-ol. 1,2-Propanediol) (C-5-B)
Apparatus:	GC/MS/DS (gas chromatograph with mass spectrometer and data system)

Analysis-Method Parameters:

GC:
Column -- Fused-silica capillary, 30 m long, 0.25-mm ID, wall-coated with SE-52
Carrier gas -- He at 25 cm/s at 100 °C
or
Column -- Carbopak C plus 0.8% THEED (tetrahydroxyethlenediamine) packed in 55 x 0.2-cm ID glass column
Carrier gas -- He
Temperature program -- 115 °C, isothermal

MS:
Mass range -- 42-450 amu
Scan range -- 2 s/scan
Ionization -- EI, 70 eV

Criteria for Qualitative Identification:	As defined in Section VI.E.3.b. (of the Methods Manual).
Criteria for Quantitative Analysis:	As defined in Section VI.E.3.c.: at least two calibration standards to be run daily.
Detection Limits:	5-20 ng of each compound injected on column or 1-4 μg/m^3 of each compound in a 5-m^3 stack-gas sample, 0.25-1 μg/g of each compound in a 20-g waste sample, 0.25-1 μg/g of each compound in a 20-g ash sample.

EXAMPLE 1. POHC ANALYSIS METHOD (continued)

References:

1. DiCorcia, A.; Samperi, R. Gas chromatographic determination of glycolo at the parts-per-million level in water by graphitized carbon black. Anal. Chem. 51(5): 776-778; 1979.

EXAMPLE 2. POHC SAMPLING METHOD

Method Number:

Method Name: Modified Method 5 (MM5)

Basic Method: Comprehensive sampling train (filter-sorbent-impinger)

Matrix: Stack gas (particulate)

Specific POHC from Appendix VIII to which method may be applied: Epinephrine (3.4-Dihydroxy-α-[(methylamine)-methyl]benzyl alcohol) (C-5-C)

Sampling-Method Parameters:

Hardware:
RAC or equivalent sampling train modified to include sorbent module as shown in Figure 3
Filter -- Glass-fiber filter
Sorbent -- Alumina (pH 8.5)
Impinger reagent -- 1% HCl solution

Deployment:
Traverse and sample isokinetically as specified in EPA Methods 1-5
Collect 5-m^3 sample at approximately 0.75-ft^3/min sampling rate

Recovery Check: Spike filter/sorbent or impingers (or both) before sampling with known quantity of deuterated or fluorinated analog of target compound.

References:

EXAMPLE 2. POHC SAMPLE-PREPARATION METHOD

Method Number:

Method Name: Desorption

Basic Method: Desorption of adsorbed compound with 0.5 M

Matrix: Sorbent material (alumina), filter
Solid waste
Fly Ash
Bottom Ash

Specific POHC from Appendix VIII to which method may be applied: Epinephrine (3,4-Dihydroxy-α-[(methylamine) methyl]benzyl alcohol) (C-5-C)

Extraction-Method Parameters: Standard solid/liquid extraction

EXAMPLE 2. POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Analyte concentration
Basic Method:	Evaporation
Matrix:	Salt solution of epinephrine
Specific POHC from Appendix VIII to which method may be applied:	Epinephrine (3,4-Dihydroxy-α-[(methylamine)-methyl]benzyl alcohol) (C-5-C)
Sampling-Method Parameters	Evaporate slowly in water bath
Recovery Check:	Add epinephrine to appropriate acid solution and evaporate by heating in water bath
References:	

EXAMPLE 2: POHC ANALYSIS METHOD

Method Number:	
Method Name:	Epinephrine (catechol amine)
Basic Method:	LCEC, Derivatization/GC/MS, or GC/FID
Matrix:	1% HCl extract of liquid and solid organic waste and sorbent 1% HCl wash solution of filter in sampling train 1% HCl impinger solution
Specific POHC from Appendix VIII to which method may be applied:	Epinephrine (3,4-Dihydroxy-α-[(methylamine)-methyl]benzyl alcohol) (C-5-C)
Apparatus:	LCEC (Liquid chromatography with electrochemical detection) or GC/MS/DS (Finnigan 4000 or equivalent)

Analysis-Method Parameters:

HPLC:

Column -- µBondapak C_{18} (Waters Associates)
Mobile phase -- 6.8 g NaAc, 100 mg EDTA, 1 g heptanesulfonic acid in 1 L, pH adjusted to 4.8 with 2 M HCl
Flow rate -- 1 mL/min
Detector type -- electrochemical detection
Injector temperature -- 250 °C

Criteria for Qualitative Identification:	As defined in Section VI.E.3.b.
Criteria for Quantitative Analysis:	As defined in Section VI.E.3.c; at least two calibration standards to be run daily.
Detection Limits:	Unspecified

EXAMPLE 2. POHC ANALYSIS METHOD (continued)

References:

1. Goldstein, D.S., et al. Validity and reliability of liquid chromatography with electrochemical detection for measuring plasma levels of norepinephrine and epinephrine in man. Life Sci. 28: 467-475; 1981.

2. Mefford, I.N., et al. Determination of plasma catecholamines and free 3,4-dihydroxyphenylacetic acid in continuously collected human plasma by high performance liquid chromatography with electrochemical detection. Life Sci. 28: 477-483; 1981.

3. Davis, G.C.; Kissinger, P.T.; Shoup, R.E. Strategies for determination of serum or plasma norepinephrine by reverse-phase liquid chromatography. Anal. Chem. 53: 156-159; 1981.

EXAMPLE 3: POHC SAMPLING METHOD

Method Number:	
Method Name:	Modified Method 5 (MM5)
Basic Method:	Comprehensive sampling train (filter-sorbent-impinger)
Matrix:	Filter or sorbent material (or both) from stack sampler and solid waste
Specific POHC from Appendix VIII to which method may be applied:	Thiols (Benzenethiol, Tetrachloromethanethiol, and Trichloromethanethiol) (C-5-A)

Sampling-Method Parameters:

Hardware:	RAC or equivalent sampling train modified to include sorbent module as shown in Figure 3 Filter -- Glass-fiber filter Sorbent -- XAD-2 resin Impinger reagent --
Deployment:	Traverse and sample isokinetically as specified in EPA Methods 1-5 Collect 5-m^3 sample at approximately 0.75-ft^3/min sampling rate
Recovery check:	Spike filter/sorbent before sampling with known quantity of deuterated or fluorinated analog of target compound.

References:

EXAMPLE 3. POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Soxhlet extraction
Basic Method:	Continuous 24-h extraction with methylene chloride
Matrix:	Solid wastes Fly ash Bottom ash Particulate/sorbent from comprehensive sampling train
Specific POHC from Appendix VIII to which method may be applied:	Thiols (Benzenethiol, Tetrachloromethanethiol, and Trichloromethanethiol) (C-5-A)
Extraction-Method Parameters:	Apparatus — Fisher Catalog No. 09-556 or equivalent Solvent — Methylene chloride, 200 mL Time — 24-h extraction Sample size — 20-200 g

EXAMPLE 3: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Extraction concentration
Basic Method:	Kuderna-Danish
Matrix:	Solvent extract
Specific POHC from Appendix VIII to which method may be applied:	Thiols (Benzenethiol, Tetrachloromethanethiol, and Trichloromethanethiol) (C-5-A)
Method Parameters:	Use Kuderna-Danish evaporative concentrator with three-ball-Snyder column to reduce extract volume to <10 mL. Use micro Snyder to concentrate further if necessary to meet detection limits.
Recovery Check:	Add these compounds to appropriate volume of solvent and concentrate using procedures applied to samples.
References:	

EXAMPLE 3: POHC ANALYSIS METHOD

Method Number:

Method Name: Thiols

Basic Method: GC/FID or GC/MS

Matrix: Organic solvent extract
Liquid organic waste (neat or diluted)

Specific POHC from Appendix VIII to which method may be applied: Thiols (Benzenethiol, Tetrachloromethanethiol, and Trichloromethanethiol) (C-5-A)

Apparatus: GC/FPD (gas chromatography with flame-photometric detection) or GC/MS

Analysis-Method Parameters:

GC: Column -- Fused-silica capillary, 30 m long, 0.25 mm ID wall-coated with SE-52
Carrier gas -- He at 25 cm/s at 100 °C
or
Column -- Aluminum packed with 30% tritolyl phosphate on Chromosorb P support

MS: Mass range -- 42-450 amu
Scan range -- 2 s/scan
Ionization -- EI, 70 eV

Criteria for Qualitative Identification: As defined in Section VI.E.3.b.

Criteria for quantitative Analysis: As defined in Section VI.E.3.c.; at least two calibration standards to be run daily.

Detection Limits: 5-20 ng of each compound injected on column or 1-4 $\mu g/m^3$ of each compound in a 5-m^3 stack-gas sample,
0.25-1 $\mu g/g$ of each compound in a 20-g waste sample,
0.25-1 $\mu g/g$ of each compound in a 20-g ash sample.

References:

1. Kremer, L.; Spicer, L.D. Gas chromatographic separation of hydrogen sulfide, carbonyl sulfide and higher sulfur compounds with a single pass system. Anal. Chem. 45(11): 1973.

EXAMPLE 4: POHC SAMPLING METHOD

Method Number:

Method Name: Modified Method 5 (MM5)

Basic Method: Comprehensive sampling train (filter-sorbent-impinger)

Matrix: Stack gas (vapor-phase material)

Specific POHC from Appendix VIII to which method may be applied: Aldehydes (Acetaldehyde, Crotonaldehyde, Glycidylaldehyde, and Chloroacetaldehyde) (C-4-C)

Sampling-Method Parameters:

Hardware:
RAC or equivalent sampling train modified to include sorbent module as shown in Figure 3
Filter -- Not applicable
Sorbent -- Not applicable
Impinger reagent -- DNPH in 2 N HCl, or 2,3,4,5,6-pentachlorobenzylhydrazine, or 10% $NaHSO_3$ (Figure 4)

Deployment:
Traverse and sample isokinetically as specified in EPA Methods 1-5
Collect 5-m^3 sample at approximately 0.75-ft^3/min sampling rate

Recovery Check: Spike impingers before sampling with known quantity of deuterated or fluorinated analog of target compound.

References:

EXAMPLE 4: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Derivatize with DNPH and extract with CH_2Cl_2 and pentane
Basic Method:	3-batch liquid-liquid phase extraction
Matrix:	Solid wastes (derivatized) Fly ash (derivatized) Impinger solution (DNPH, 2 N HCl)
Specific POHC from Appendix VIII to which method may be applied:	Aldehydes (Acetaldehyde, Crotonaldehyde, Glycidylaldehyde, and Chloroacetaldehyde) (C-4-C)
Extraction-Method Parameters:	Apparatus — Standard equipment Solvent — Methylene chloride, 100 mL, and n-pentane, 100 mL Time — Sample size — 20-200 g

EXAMPLE 4: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Extraction concentration
Basic Method:	Kuderna-Danish
Matrix:	Solvent extracts
Specific POHC from Appendix VIII to which method may be applied:	Aldehydes (Acetaldehyde, Crotonaldehyde, Glycidylaldehyde, and Chloroacetaldehyde) (C-4-C)
Method Parameters:	Use Kuderna-Danish evaporative concentrator with three-ball-Snyder column to reduce extract volume to <10 mL. Use micro Snyder to concentrate further if necessary to meet detection limits.
Recovery Checks:	Add compound of interest to appropriate volume of solvent and concentrate using procedures applied to samples.
References:	

EXAMPLE 4: POHC-ANALYSIS METHOD

Method Number:	
Method Name:	Aldehydes
Basic Method:	Derivatization (DNPH) and HPLC/UV or GC/ECD or GC/MS
Matrix:	Organic solvent extract of derivative Liquid organic waste (neat or diluted) (derivatized)
Specific POHC from Appendix VIII to which method may be applied:	Aldehydes (Acetaldehyde, Crotonaldehyde, Glycidylaldehyde, and Chloroacetaldehyde) (C-4-C)
Apparatus:	HPLC/UV (254 nm or 370 nm), GC/ECD (gas chromatography with electron-capture detection), or GC/MS/DS (Finnigan 4000 or equivalent)

Analysis-Method Parameters:

GC:	Column — Fused-silica capillary, 30 m long, 0.25-mm ID wall-coated with SE-52 Carrier gas — He at 25 cm/s at 100 °C Temperature program — 25 °C, 2 min isothermal 25-150 °C at 4 °C/min Injector temperature — 200 °C
HPLC:	Column — Zorbax-ODS 1250 x 4.6-mm ID 75% CH_3OH/25% H_2O)
MS:	Mass range — 42-450 amu Scan rate — 2 s/scan Ionization — EI, 70 eV

Criteria for Qualitative Identification:	As defined in Section VI.E.3.b.
Criteria for Quantitative Analysis:	As defined in Section VI.E.3.c.; at least two calibration standards to be run daily.

Detection Limits: 5-20 ng of each compound injected on column or 1-4 μg/m^3 of each compound in a 5-m^3 stack-gas sample.
0.25-1 μg/g of each compound in a 20-g waste sample,
0.25-1 μg/g of each compound in a 20-g ash sample.

References:

1. Kobayashi, K., et al. Gas chromatography determination of low-molecular-weight carbonyl compounds in aqueous solution as their *o*-(2,3,4,5,6-pentafluorobenzyl) oximes. J. Chromatogr. 187: 413-17; 1980.

EXAMPLE 5: POHC SAMPLING METHOD

Method Number:

Method Name: Modified Method 5 (MM5)

Basic Method: Comprehensive sampling train (filter-sorbent-impinger)

Matrix: Stack gas (vapor phase material)

Specific POHC from Appendix VIII to which method may be applied: Phosphate and thiophosphate esters (O,O-Diethyl-S-methylester phosphorodithioic acid; O-p-Nitrophenylester, O,O-Diethyl phosphoric acid; O,O-Diethyl-O-(2-pyrazinyl)phosphorothioate; Diisopropyl fluorophosphate; Tetraethyldithio pyrophosphate; Tetraethyl pyrophosphate; O,O,O-Triethyl phosphorothioate; Tris(2,3-dibromopropyl)phosphate; Hexaethyl tetraphosphate; and Phosphorothioic acid-O,O-dimethylester, O-ester with N,N-dimethyl benzene sulfonamide)

Sampling-Method Parameters:

Hardware: RAC or equivalent sampling train modified to include sorbent module as shown in Figure 3
Filter — Glass-fiber filter
Sorbent — XAD-2 resin
Impinger reagent — Water

Deployment: Traverse and sample isokinetically as specified in EPA Methods 1-5
Collect 5-m^3 sample at approximately 0.75-ft^3/min sampling rate

Recovery Check: Spike sorbent or impingers (or both) before sampling with known quantity of deuterated or fluorinated analog of target compound.

References:

EXAMPLE 5: POHC SAMPLE-PREPARATION METHOD

Method Number:

Method Name: Soxhlet extraction

Basic Method: Continuous 24-h extraction with methylene chloride

Matrix:
Solid wastes
Fly ash
Particulate (glass fiber filter)

Specific POHC from Appendix VIII to which method may be applied: Phosphate and thiophosphate esters (*O*,*O*-Diethyl-*S*-methylester phosphorodithioic acid; *O*-*p*-Nitrophenylester, *O*,*O*-Diethyl phosphoric acid; *O*,*O*-Diethyl-*O*-(2-pyrazinyl)phosphorothioate; Diisopropyl fluorophosphate; Tetraethyldithio pyrophosphate; Tetraethyl pyrophosphate; *O*,*O*,*O*-Triethyl phosphorothioate; Tris(2,3-dibromopropyl)phosphate; Hexaethyl tetraphosphate; and Phosphorothioic acid-*O*,*O*-dimethylester, *O*-ester with *N*,*N*-dimethyl benzene sulfonamide)

Extraction-Method Parameters:

Apparatus — Fisher Catalog No. 09-556 or equivalent
Solvent — Methylene chloride, 200 mL
Time — 24-h extraction
Sample size — 20-200 g

EXAMPLE 5. POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Extraction concentration*
Basic Method:	Kuderna-Danish
Matrix:	Solvent extracts
Specific POHC from Appendix VIII to which method may be applied:	Phosphate and thiophosphate esters (*O*,*O*-Diethyl-*S*-methylester phosphorodithioic acid; *O*-*p*-Nitrophenylester, *O*,*O*-Diethyl phosphoric acid; *O*,*O*-Diethyl-*O*-(2-pyrazinyl)phosphorothioate; Diisopropyl fluorophosphate; Tetraethyldithio pyrophosphate; Tetraethyl pyrophosphate; *O*,*O*,*O*-Triethyl phosphorothioate; Tris(2,3-dibromopropyl)phosphate; Hexaethyl tetraphosphate; and Phosphorothioic acid-*O*,*O*,-dimethylester, O-ester with *N*,*N*,-dimethyl benzene sulfonamide)
Method Parameters:	Use Kuderna-Danish evaporative concentrator with three ball-Snyder column to reduce extract volume to <10 mL. Use micro Snyder to concentrate further if necessary to meet detection limits.
Recovery Check:	Add compound of interest to appropriate volume of solvent and concentrate using procedures applied to samples.
References:	

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*Volatile components like tetraethyl pyrophosphate will be lost in this extract concentration procedure. Lower recoveries resulting in higher detection limits might have to be accepted in this case.

EXAMPLE 5: POHC ANALYSIS METHOD

Method Number:	
Method Name:	Phosphate and thiophosphate esters
Basic Method:	GC/AFID or FPD or GC/MS
Matrix:	Methylene chloride extract Liquid organic waste (neat or diluted)
Specific POHC from Appendix VIII to which method may be applied:	Phosphate and thiophosphate esters (*O*,*O*-Diethyl-*S*-methylester phosphorodithioic acid; *O*-*p*-Nitrophenylester, *O*,*O*-Diethyl phosphoric acid; *O*,*O*-Diethyl-*O*-(2-pyrazinyl)phosphorothioate; Diisopropyl fluorophosphate; Tetraethyldithio pyrophosphate; Tetraethyl pyrophosphate; *O*,*O*,*O*-Triethyl phosphorothioate; Tris(2,3-dibromopropyl)phosphate; Hexaethyl tetraphosphate; and Phosphorothioic acid-*O*,*O*-dimethylester, *O*-ester with *N*,*N*-dimethyl benzene sulfonamide)
Apparatus:	GC/AFID (gas chromatography with alkali flame-ionization detection) or GC/MS/DS (Finnigan 4000 or equivalent)

Analysis-Method Parameters:

GC:
Column — Fused-silica capillary, 3 m long, 0.25-mm ID wall-coated with SE-52
Carrier gas — He at 25 cm/s at 100 °C
Temperature program — 25 °C, 2 min isothermal
40-250 °C at 4 °C/min

MS:
Mass range — 42-450 amu
Scan rate — 2 s/scan
Ionization — EI, 70 eV

Criteria for Qualitative Identification:	As defined in Section VI.E.3.b.
Criteria for Quantitative Analysis:	As defined in Section VI.E.3.c.; at least two calibration standards to be run daily.

EXAMPLE 6: POHC SAMPLING METHOD

Method Number:

Method Name: Modified Method 5 (MM5)

Basic Method: Comprehensive sampling train (filter-sorbent-impinger)

Matrix: Stack gas (particulate plus vapor phase material)

Specific POHC from Appendix VIII to which method may be applied: Sulfates and sulfonates (Dimethyl sulfate, Ethyl methanesulfonate, Methyl methanesulfonate) (C-4-E)

Sampling-Method Parameters:

Hardware: RAC or equivalent sampling train modified to include sorbent module as shown in Figure 3
Filter — Glass-fiber filter (acid washed)
Sorbent — XAD-2 resin, Porapak Q, or silica gel

Deployment: Traverse and sample isokinetically as specified in EPA Methods 1-5
Collect 5-m^3 sample approximately 0.75-ft^3/min sampling rate

Recovery Check: Spike filter or sorbent (or both) before sampling with known quantity of deuterated or fluorinated analog of target compound.

References:

1. Lee, M.L.; Later, D.W.; Rollin, D.L.; Eatough, D.J.; Hansen, D.L. Dimethyl and monomethyl sulfate: Presence in fly ash and airborne particulate matter. Science 207: 186-188; 1980.

EXAMPLE 6: POHC SAMPLE-PREPARATION METHOD

Method Number:

Method Name: Soxhlet extraction

Basic Method: Continuous 24-h extraction with acetone (glass-fiber filter and Porapak Q) or water (glass-fiber filter and silica gel)

Matrix:
Solid wastes
Fly ash
Bottom ash
Particulate and sorbent from comprehensive sampling train

Specific POHC from Appendix VIII to which method may be applied: Sulfates and sulfonates (Dimethyl sulfate, Ethyl methanesulfonate, Methyl methanesulfonate) (C-4-E)

Extraction-Method Parameters:

Apparatus — Fisher Catalog No. 09-556 or equivalent
Solvent — Acetone (Porapak Q as sorbent)
Water (silica gel as sorbent)
Time — 25-h continuous extraction
Sample size — 20-200 g

EXAMPLE 6: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Extract concentration*
Basic Method:	Kuderna-Danish
Matrix:	Solvent extracts
Specific POHC from Appendix VIII to which method may be applied:	Sulfates and sulfonates (Dimethyl sulfate, Ethyl methanesulfonate, Methyl methanesulfonate) (C-4-E)
Method Parameters:	Use Kuderna-Danish evaporation concentrator with three ball-Snyder column to reduce extract volume to <10 mL. Use micro Snyder to concentrate further if necessary to meet detection limits.
Recovery Check:	Add compounds of interest to appropriate volume of solvent and concentrate using procedures applied to samples.
References:	

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*Only for the acetone extract.

EXAMPLE 6: POHC ANALYSIS METHOD

Method Number:

Method Name: Sulfates and sulfonates

Basic Method: GC/MS

Matrix: Organic solvent extract
Water extract
Liquid organic waste

Specific POHC from Appendix VIII to which method may be applied: Sulfates and sulfonates (Dimethyl sulfate, Ethyl methanesulfonate, Methyl methanesulfonate) (C-4-E)

Apparatus: GC/MS/DS (Finnigan 4000 or equivalent)

Analysis-Method Parameters:

GC:
Column — Fused-silica capillary, 3 m long, 0.25-mm ID, wall-coated with SE-52
Carrier gas — He at 25 cm/s at 100 °C
Temperature program — 50 °C, 8 min isothermal
50-150 °C at 8 °C/min
Injector temperature — 150 °C

MS:
Mass range — 42-450 amu
Scan rate — 2 s/scan
Ionization — EI, 70 eV

Criteria for Qualitative Identification: As defined in Section VI.E.3.b.

Criteria for Quantitative Analysis: As defined in Section VI.E.3.c.; at least two calibration standards to be run daily.

Detection Limits: 5-20 ng of each compound injected on column or 1.4 μg/m^3 of each compound in a 5-m^3 stack-gas sample,
0.25-1 μg/g of each compound in a 20-g waste sample,
0.25-1 μg/g of each compound in a 20-g ash sample.

EXAMPLE 7: POHC SAMPLING METHOD

Method Number:

Method Name: Modified Method 5 (MM5)

Basic Method: Comprehensive sampling train (filter-sorbent-impinger)

Matrix: Stack gas (particulate plus vapor-phase material)

Specific POHC from Appendix VIII to which method may be applied: Trifluoroacetic acid, Na salt (C-4-F)

Sampling-Method Parameters:

Hardware: RAC or equivalent sampling train modified to include sorbent module as shown in Figure 3
Filter — Glass-fiber filter
Impinger reagent — 1% HNO_3 solution

Deployment: Traverse and sample isokinetically as specified in EPA Methods 1-5
Collect 5-m^3 sample at approximately 0.75-ft^3/min sampling rate

Recovery Check: Spike filter or impingers (or both) before sampling with known quantity of acetic acid analog of target compound.

References:

EXAMPLE 7: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Solvent extraction
Basic Method:	3-batch extraction with 1% HNO_3
Matrix:	Solid wastes Fly ash Bottom ash Particulate (glass-fiber filter)
Specific POHC from Appendix VIII to which method may be applied:	Trifluoroacetic acid, Na salt (C-4-F)
Extraction-Method Parameters:	
	Apparatus — Flask and wrist shaker Solvent — 1% HNO_3, 200 mL Time — 3 x 0.25 h Sample size — 20-200 g

EXAMPLE 7: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Purge and trap or steam distillation
Basic Method:	Purge or steam distillation
Matrix:	1% HNO_3
Specific POHC from Appendix VIII to which method may be applied:	Trifluoroacetic acid, Na salt (C-4-F)
Method Parameters:	Purging device, trap and desorber (15 cm of Tenax-GC, 60/80 mesh)
Recovery Check:	Add trifluoroacetic acid to 1% HNO_3 solution to appropriate volume and purge and trap or steam distillation

References:

1. EPA Method 624 (purge and trap).

EXAMPLE 7: POHC ANALYSIS METHOD

Method Number:

Method Name: Trifluoroacetic acid

Basic Method Derivatization with p-bromobenzyl bromide and GC/ECD or MS

Matrix: Acidified water extract

Specific POHC from Appendix VIII to which method may be applied: Trifluoroacetic acid, Na salt (C-4-F)

Apparatus: GC/ECD or GC/MS/DS (Finnigan 4000 or equivalent

Analysis-Method Parameters:

GC:
- Column — Fused-silica capillary column, 30 m long, 0.25-mm ID, wall-coated with SE-52
- Carrier gas — He at 25 cm/s at 100 °C (linear velocity)
- Temperature program — 25 °C, 2 min isothermal
  - 25-100 °C at 8 °C/min
- Injector temperature — 200 °C

MS:
- Mass range — 42-450 amu
- Scan rage — 2 s/scan
- Ionization — EI, 70 eV

Criteria for Qualitative Identification: As defined in Section VI.E.3.b.

Criteria for Quantitative Analysis: As defined in Section VI.E.3.c.; at least two calibration standards to be run daily.

Detection Limits:
<5 ng of derivative injected on column
<1 μg/m^3 in a 5-m^3 stack-gas sample
<0.25 μg/g in a 20-g waste sample
<5 μg/L in a 1-L scrubber water sample
<0.25 μg/g in a 20-g ash sample

References:

EXAMPLE 8: POHC SAMPLING METHOD

Method Number:

Method Name: Modified Method 5 (MM5)

Basic Method: Comprehensive sampling train (filter-sorbent-impinger)

Matrix: Stack gas (vapor-phase material)

Specific POHC from Appendix VIII to which method may be applied: Methyl methacrylate (C-4-D)

Sampling-Method Parameters:

Hardware: RAC or equivalent sampling train modified to include sorbent module as shown in Figure 3
Sorbent — XAD-2 resin

Deployment: Traverse and sample isokinetically as specified in EPA Methods 1-5
Collect 5-m^3 sample at approximately 0.75-ft^3/min sampling rate

Recovery Check: Spike sorbent before sampling with known quantity of deuterated or fluorinated analog of target compound.

References:

EXAMPLE 8: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Soxhlet extraction
Basic Method:	Continuous 24-h extraction with *n*-pentane (CH_2Cl_2 will also be effective)
Matrix:	Solid wastes Sorbent from comprehensive sampling train
Specific POHC from Appendix VIII to which method may be applied:	Methyl methacrylate (c-4-D)
Extraction-Method Parameters:	Apparatus — Fisher Catalog No. 09-556 or equivalent Solvent — *n*-pentane, 200 mL Time — 24-h extraction Sample size — 20-200 g

EXAMPLE 8: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Extract concentration*
Basic Method:	Kuderna-Danish
Matrix:	Solvent extracts
Specific POHC from Appendix VIII to which method may be applied:	Methyl methacrylate (C-4-D)
Method Parameters:	Use Kuderna-Danish evaporative concentrator with three ball-Snyder column to reduce extract volume to <10 mL. Use micro Snyder to concentrate further if necessary to meet detection limits.
Recovery Check:	Add methyl methacrylate to appropriate volume of solvent and concentrate using procedures applied to samples.
References:	

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*Lower temperatures should be used in this step because of the relatively low boiling point of methyl methacrylate.

EXAMPLE 8: POHC ANALYSIS METHOD

Method Number:

Method Name: Methyl methacrylate

Basic Method: GC/FID, GC/MS

Matrix:
Organic solvent extract
Liquid organic waste (neat or diluted)
Gas grab sample

Specific POHC from Appendix VIII to which method may be applied: Methyl methacrylate (C-4-D)

Apparatus: GC/FID, GC/MS/DS (Finnigan 4000 or equivalent)

Analysis-Method Parameters:

GC:
Column — Fused-silica capillary, 30-m-long, 0.25-mm ID, with SE-52
Carrier gas — He at 25 cm/s at 100 °C
Temperature program — 50 °C, 8 min isothermal
50-150 °C at 8 °C/min
Injector temperature — 150 °C

MS:
Mass range — 42-450 amu
Scan rate — 2 s/scan
Ionization — IE, 70 eV

Criteria for Qualitative Identification: As defined in Section VI.E.3.b.

Criteria for Quantitative Analysis: As defined in Section VI.E.3.c.; at least two calibration standards to be run daily.

Detection Limits:
5-20 ng of each compound injected on column or 1-4 μg/m^3 of each compound in a 3-m^3 stack-gas sample,
0.25-1 μg/g of each compound in a 20-g waste sample,
0.25-1 μg/g of each compound in a 20-g ash sample.

References:

1. Rygle, K.G. Trace residual monomer analysis by capillary gas chromatography. J. Coat. Technol. 52: 47-52; 1980.

EXAMPLE 9: POHC SAMPLING METHOD

Method Number:

Method Name: Modified Method 5 (MM5)

Basic Method: Comprehensive sampling train (filter-sorbent-impinger)

Matrix: Stack gas (particulate)

Specific POHC from Appendix VIII to which method may be applied: Carboxylic acids (1-*p*-chlorobenzyl)-5-methoxyl-2-methylindone-3-acetic acid, 7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, 2,4-Dichlorophenoxyacetic acid, 2,4,5-Trichlorophenoxyacetic acid, and 2-(2,4,5-Trichlorophenoxy)propionic acid)

Sampling-Method Parameters:

Hardware: RAC or equivalent sampling train modified to include sorbent module as shown in Figure 3
Filter — Glass-fiber filter
Sorbent — Not applicable
Impinger reagent — Not applicable

Deployment: Traverse and sample isokinetically as specified in EPA Methods 1-5
Collect 5-m^3 sample at approximately 0.75-ft^3/min sampling rate

Recovery Check: Spike filter before sampling with known quantity of deuterated or fluorinated analog of target compound.

References:

EXAMPLE 9: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Soxhlet extraction
Basic Method:	Continuous 24-h extraction with diethyl ether
Matrix:	Solid wastes Fly ash Bottom ash Particulate from comprehensive sampling train
Specific POHC from Appendix VIII to which method may be applied:	Carboxylic acids (1-p-chlorobenzyl)-5-methoxyl-2-methylindone-3-acetic acid, 7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, 2,4-Dichlorophenoxyacetic acid, 2,4,5-Trichlorophenoxyacetic acid, and 2-(2,4,5-Trichlorophenoxy)propionic acid)

Extraction-Method Parameters:

Apparatus — Fisher Catalog No. 09-556 or equivalent
Solvent — Methylene chloride, 200 mL
Time — 24-h extraction
Sample size — 20-200 g

EXAMPLE 9: POHC SAMPLE-PREPARATION METHOD

Method Number:	
Method Name:	Extract concentration
Basic Method:	Kuderna-Danish
Matrix:	Solvent extracts
Specific POHC from Appendix VIII to which method may be applied:	Carboxylic acids (1-*p*-chlorobenzyl)-5-methoxyl-2-methylindone-3-acetic acid, 7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, 2,4-Dichlorophenoxyacetic acid, 2,4,5-Trichlorophenoxyacetic acid, and 2-(2,4,5-Trichlorophenoxy)propionic acid)
Method Parameters:	Use Kuderna-Danish evaporative concentrator with three ball-Snyder column to reduce extract volume to <10 mL. Use micro Snyder to concentrate further if necessary to meet detection limits.
Recovery Check:	Add components of this group (C-4-A) to appropriate volume of solvent and concentrate using procedures applied to samples.
References:	

EXAMPLE 9: POHC ANALYSIS METHOD

Method Number:	
Method Name:	Carboxylic acids
Basic Method:	Derivatization* GC/ECD or GC/MS
Matrix:	Diethyl ether extract Liquid organic waste (neat or diluted)
Specific POHC from Appendix VIII to which method may be applied:	Carboxylic acids (1-*p*-chlorobenzyl)-5-methoxyl-2-methylindone-3-acetic acid, 7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, 2,4-Dichlorophenoxyacetic acid, 2,4,5-Trichlorophenoxyacetic acid, and 2-(2,4,5-Trichlorophenoxy)propionic acid)
Apparatus:	GC/ECD or GC/MS/DS (Finnigan 4000 or equivalent)

Analysis-Method Parameters:

GC:
Column — Fused-silica capillary, 30 m long, 0.25-mm ID, wall-coated with SE-52
Carrier gas — He at 25 cm/s at 100 °C (GC/MS)
5% methane in argon
Temperature program — 40 °C, 2 min isothermal
40-250 °C at 20 °C/min
Injector temperature — 250 °C

MS:
Mass range — 42-450 amu
Scan rate — 2 s/scan
Ionization — EI, 70 eV

Criteria for Qualitative Identification:	As defined in Section VI.E.3.b.
Criteria for Quantitative Analysis:	As defined in Section VI.E.3.c.; at least two calibration standards to be run daily.

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*Derivatization with either diazomethane or an extractive alkylation procedure is necessary to form the ester.

EXAMPLE 9. POHC ANALYSIS METHOD (continued)

Detection Limits:	5-20 ng of each compound injected on column or 1-4 $\mu g/m^3$ of each compound, in a 5-m^3 stack-gas sample, 0.25-1 $\mu g/g$ of each compound in a 20-g waste sample, 0.25-1 $\mu g/g$ of each compound in a 20-g ash sample.

References:

1. ASTM Method D3478-79, Chlorinated phenoxy acid herbicides in water.

2. Plazonnet, B.; Vandenheuval, W.J.A. Preparation, gas chromatography and mass spectrometry of methyl and trimethyl silyl esters in indomethacin. J. Chromatogr. 142: 587-596; 1977.

3. Ferry, D.G., et al. Indomethacin estimatioN IN plasma and serum by electron capture gas chromatography. J. Chromatogr. 89: 110-112; 1974.

4. Arbin, A. Three alkylation methods for the detemrination of indomethacin in plasma by electron capture gas chromatography. J. Chromatogr. 144: 85-92; 1977.

5. Jensen, J.M. Detemrination of indomethacin in serum by an extractive alkylation tyechnique and gas-liquid chromatography. J. Chromatogr. 153: 195-202; 1978.

In laboratory work performed after the compilation of these proposed methods, we at SoRI developed several analysis methods that are believed to be more suitable than the corresponding proposed procedures. For example, an HPLC/UV analysis method was developed for the determination of phenoxyacetic acids that does not require the derivatization step of the GC/MS technique proposed in Table D-1. Many of the proposed analysis methods and all of the proposed sampling procedures, however, still represent viable techniques that should be considered for inclusion of the revised Methods Manual.

REVISION OF THE GENERAL SAMPLE DIGESTION PROCEDURE AND SPECIFIC ANALYSIS METHODS FOR THE DETERMINATION OF METALS

An editorial and technical revision of sample operation and analysis methods for metals was undertaken as a refinement of those procedures given in the Methods Manual. The resulting recommended revisions are present on pages 283 through 287. Comments on the digestion and specific analysis procedures are given initially. Following these comments, revised methods, which include many of the suggested changes, are given on pages 288 through 302 for antimony, arsenic, barium, beryllium, cadmiun, chromium, lead, nickel, selenium, strontium, silver, thallium, and vanadium.

EVALUATION OF DIGESTION AND ANALYSIS PROCEDURES FOR BERYLLIUM, STRONTIUM, AND VANADIUM

The general digestion procedure delineating the preparation of water, sludge, and solid samples for the subsequent determination of metals had not previously been verified for beryllium, strontium, and vanadium. Consequently, soil and water samples were spiked with salts of these metals and subjected to the digestion procedure.

GENERAL SAMPLE DIGESTION PROCEDURES

1. Pg VI-51 "Aliquots (100 g or 100 ml) from well mixed field samples... will be used for the analysis of metals".

    A. The methods cited state to use 3 ml of concentrated nitric acid on the 100 g of sample. If the sample is primarily solid, 3 ml of acid will not wet the sample and will not adequately digest the sample. A smaller aliquot (5-10 g) should be taken for samples that are primarily solids. The referenced cited (SW-846) does state that 100 g or 100 ml aliquots should be used for As, Cd, Ni, and Se. These methods should be corrected for cases where high solids samples are to be analyzed.

2. Pg VI-51 "Thorium (Th)"

    A. I believe that thallium (Tl) should be listed here in place of thorium (Th). Thallium is a priority pollutant metal and is listed under RCRA, whereas thorium is not. Furthermore, the individual methods included in the manual include one for thallium, but not for thorium.

3. Pg VI-51 "Most samples will be prepared for analysis by general HNO_3 digestion procedures as specified in the methods for each metal in SW-846, section 8, methods 8.50 to 8.60".

    A. No method exists in SW-846 for beryllium, osmium, strontium, thallium (see No. 2) or vanadium, thus this reference is incomplete.

    B. The methods given in SW-846 for arsenic and selenium involve HNO_3- H_2O_2 digestion, not just nitric acid.

4. Pg VI-51 "Pesticide waste samples containing high levels of organic materials, such as oil, greases or waxes, will be prepared by dissolving the sample in an appropriate organic solvent or digesting the sample in nitric acid, sulfuric acid, hydrogen peroxide, and hydrochloric acid as specified in SW-846, Section 8, pages 8.49-7 to 8.49-11".

    A. As stated in SW-846, pages 8.49-7 to 8.49-11. The HNO_3-H_2SO_4-H_2O_2-HCl digestion is appropriate for As, Se, Hg, Cr, Cd, Ba, Pb, and Ag. If a precipatate forms, special precautions are required for Ba, Pb, and

(continued)

Ag since the formation of $BaSO_4$, $PbSO_4$, or AgCl can occur if the cation concentrations are high enough to exceed the solubility product constant. However, this procedure is not listed for analysis of antimony, beryllium, nickel, osmium, strontium, thallium (see No. 2), or vanadium. Thus, no method is provided for analysis of these elements in samples containing high levels of organics.

5. Pg VI-51 "Other sample preparation procedures are given in the references".

   A. The only reference given is to "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-0200 (March 1979). These methods are not applicable, in general, to samples containing high levels of organic material.

INDIVIDUAL METHODS OF ANALYSIS

1. Pg VI-139, Antimony

   A. Under apparatus, hydride generator should be included since antimony forms a hydride and this is a very sensitive method for antimony analysis.

   B. Under AA wavelength, either 206.8 nm or 231.1 nm should be specified as alternate wavelengths if high concentrations of lead are present since the lead line at 217.0 nm can interfere.

   C. Background correction should be required for graphite furnace analysis.

   D. For complex samples, the method of standard additions should be required for graphite furnace analysis.

   E. From personal experience, the HNO_3 digestion does not provide quantitative recovery of spikes in many cases. We have had much better luck using the HNO_3-H_2O_2 digestion specified for arsenic and selenium.

   F. The ICAP detection limits can be improved dramatically if hydride generation--ICAP is used.

   G. References are missing.

2. Pg VI-141, Arsenic

   A. There are many ways to form a hydride other than using $SnCl_2$ and zinc metal. The most common method is to add $NaBH_4$. Other methods should be included, if one is being specified.

   B. The ashing temperature of 1100°C for arsenic should only be used if nickel has been added to the sample to prevent atomization of arsenic. This step should be included in the method write-up.

(continued)

C. Arsenic can be analyzed by ICAP, and this method should be included, along with the corresponding detection limits and working range.

D. Hydride generation--ICAP can also be used for arsenic.

E. Background correction is required for graphite furnace work.

F. For complex samples, the method of standard additions should be required for graphite furnace analysis.

3. Pg VI-143, Barium

A. Background correction may prove useful in graphite furnace analysis, if appropriate background corrector is available at 553.6 nm (Tungsten Iodide lamp).

B. The method of standard additions is required for complex samples when using graphite furnace analysis.

C. References are missing.

4. Pg VI-145, Beryllium

A. Background correction and standard additions is required for graphite furnace work.

B. References are missing.

5. Pg VI-147, Cadmium

A. Same as 4A.

B. Reference 3, to ARL product literature, is inappropriate, particularly since no indication is given as to what information was taken from that source.

6. Pg VI-148, Chromium and Pg VI-153, Nickel

A. Same as 4A.

B. Same as 5B.

7. Pg VI-149, Lead

A. Same as 4A.

B. References are missing.

C. Lead can be determined by hydride generation--ICAP with detection limits approximately one-tenth of direct aspiration ICAP.

(continued)

8. Pg VI-151, Mercury

   A. Mercury can be determined by hydride generation ICAP with a detection limit of approximately 2 μg/ℓ. It does not form a hydride, but can be reduced to the elemental form with $NaBH_4$.

9. Pg VI-155, Osmium

   A. Same as 4A.

   B. References required.

10. Pg VI-157, Selenium

   A. There are many ways to form the hydride other than $SnCl_2$-Zinc. Other options should be specified.

   B. The ashing temperature of 1200°C can only be used if nickel has been added to the samples to prevent atomization of selenium. This step should be included in the method write-up.

   C. Selenium can be analyzed by ICAP, and this method should be included, along with the corresponding detection limits and working range.

   D. Hydride generation--ICAP can also be used for selenium.

   E. For complex samples, background correction and standard additions should be required for graphite furnace analysis.

   F. References required.

11. Pg VI-159, Silver

   A. Silver does not form a hydride, thus listing a hydride generator under apparatus is incorrect.

   B. Same as 4A.

   C. References required.

12. Pg VI-161, Strontium

   A. Strontium does not form a hydride, thus no hydride generation should be listed under apparatus.

   B. Same as 4A.

   C. Same as 5B.

(continued)

13. Pg VI-162, Thallium

    A. Thallium does not form a hydride, thus no hydride generator should be listed under apparatus.

    B. Same as 4A.

    C. Same as 5B.

    D. Under furnace parameters, dry temperature is given as 1250°C, should be 125°C.

14. Pg VI-164, Vanadium

    A. Vanadium does not form a hydride, thus no hydride generator should be listed under apparatus.

    B. Same as 4A.

    C. References required.

The following pages correspond to the pages in the Methods Manual discussed in the previous editorial and technical comments; appropriate revisions have been made or indicated.

Method Number: P032

Method Name: Digestion Procedures for Metals

Basic Method: Acid Digestion

Matrix: Aqueous
Sludge
Solid

Specific POHC/PIC from Appendix VIII to which the method may be applied:

Antimony (Sb)
Arsenic (As)
Barium (Ba)
Beryllium (Be)*
Cadmium (Cd)
Chromium (Cr)
Lead (Pb)
Mercury (Hg)
Nickel (Ni)
Osmium (Os)
Selenium (Se)
Silver (Ag)
Strontium (Sr)*
Thallium (Tl)*
Vanadium (V)*

Method Parameters:

Aliquots (100g or 100 mL or 5-10 g if sample is primarily solid) from well mixed field samples (Methods P001-P003; wastewater, sludge, and solids) will be used for the analysis of metals.

Most samples will be prepared for analysis by general HNO_3 digestion procedures as specifed in the methods for Sb, Ba, Cd, Cr, Pb, Hg, Ni, and Ag in SW-846, Section 8, Methods 8.50 to 8.60 and by $HNO_3-H_2O_2$ for As, Se, and Sb. Pesticide waste samples containing high levels of organic materials, such as oil, greases or waxes will be prepared by dissolving the sample in an appropriate organic solvent or digesting the sample in nitric acid, sulfuric acid, hydrogen peroxide and hydrochloric acid as specified in SW-846, Section 8, pages 8.49-7 to 8.49-11. Special precautions, however, should be taken if $BaSO_4$, $PbSO_4$, or AgCl precipitated.

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* These elements were not included in Method SW-846 list. However, the method was found to be applicable to them based on work in Battelle laboratories.

Method Number: A221

Method Name: Antimony

Basic Method: Atomic Spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber waters

Specific POHC/PIC from Appendix VIII to which method may be applied:

Antimony
Antimony Compounds N.O.S.

Apparatus: ICAP Spectrometer
AA Spectrometer with burner and graphite furnace
Hydride generator

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 206.8 and 187.1 nm

AA: Analytical Wavelength - 217.6 nm
206.8 nm or 231.1 nm if Pb is present at high concentration

Furnace Parameters - Dry @ 125°C for 30 sec
Ash @ 800°C for 30 sec
Atomize @ 2700°C for 10 sec
Argon gas purge
Background correction

Flame Conditions - Air - acetylene flame
flue lean

Detection Limits and Typical Working Range:

ICAP: 0.1 mg/L; 0.5-100 mg/L and less if hydride generator is used
Furnace AA: 3 μg/L; 20-300 μg/L
Flame AA: 0.2 mg/L; 1-40 mg/L

Method Number:	A222
Method Name:	Arsenic
Basic Method:	Atomic Spectroscopy
Matrix:	Solid and liquid wastes Solid effluents Scrubber water

Specific POHC/PIC from Appendix VIII to which method may be applied:

Arsenic
Arsenic compounds N.O.S.
Arsenic acid
Arsenic pentoxide
Arsenic trichloride
Benzene arsonic acid
Dichloro phenyl arsine
Diethyl arsine

Apparatus:	AA spectrophotometer Hydride generator Graphite furnace

Analysis Method Parameters:

AA: Analytical Wavelength - 193.7 nm

Hydride Generation:

In generator add $SnCl_2$ to form trivalent arsenic, then add zinc metal to form hydride. $NaBH_4$ can also be used to generate the hydride.

Flame Conditions - Argon - hydrogen flame

Furnace Parameters - Dry @ 125°C for 30 sec
Ash @ 1100°C for 30 sec (if nickel has been added to prevent atomization of arsenic)
Atomize @ 2700°C for 10 sec
Argon purge
Background correction

Method Number: A223

Method Name: Barium

Basic Method: Atomic spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber water

Specific POHC/PIC from Appendix VIII to which method may be applied:

Barium
Barium compounds N.O.S.

Apparatus: ICAP spectrometer
AA spectrometer with burner and graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelength - 455.4, 233.5 nm

AA: Analytical Wavelength - 553.6 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 1200°C - 30 sec
Atomize 2800°C - 10 sec
Argon purge gas
Background correction (Tungsten Iodide lamp)

Flame Conditions - Nitrous oxide - acetylene
Fuel rich

Detection Limits:

ICAP: 2 μg/L; 0.010-10 mg/L
Furnace: 2 μg/L; 10-200 μg/L
Flame AA: 0.1 mg/L; 1-20 mg/L

Method Number: A224

Method Name: Beryllium

Basic Method: Atomic spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber water

Specific POHC/PIC from Appendix VIII to which method may be applied:

Beryllium
Beryllium compounds N.O.S.

Apparatus: ICAP spectrophotometer
AA spectrophotometer with burner and graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 313.0, 234.9 nm

AA: Analytical Wavelength - 234.9 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 1000°C - 30 sec
Atomize 2800°C - 10 sec
Argon purge gas
Background correction

Flame Conditions - Nitrous oxide - acetylene
Fuel rich

Detection Limits:

ICAP:	0.5 μg/L; 0.005-5 mg/L
Furnace AA:	0.2 μg/L; 1-30 μg/L
Flame AA:	5 μg/L; 0.05-2 mg/L

Method Number: A225

Method Name: Cadmium

Basic Method: Atomic spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber water

Specific POHC/PIC from Appendix VIII to which method may be applied:

Cadmium
Cadmium compounds N.O.S.

Apparatus:

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelength - 226.5, 214.4 nm

AA: Analytical Wavelength - 228.8 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 500°C - 30 sec
Atomize 1900°C - 10 sec
Argon purge gas
Background correction

Flame Conditions - Air - acetylene
Oxidizing

Detection Limits:

ICAP: 0.02 mg/L; 0.1-20 mg/L
Furnace AA: 0.1 μg/L; 0.5-10 μg/L
Flame AA: 5 μg/L; 0.05-2 mg/L

References:

1. U.S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," Report No. SW-846 (1980).

2. U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979).

Method Number:	A226
Method Name:	Chromium
Basic Method:	Atomic spectroscopy
Matrix:	Solid and liquid wastes Solid effluents Scrubber water

Specific POHC/PIC from Appendix VIII to which method may be applied:

Chromium
Chromium compounds N.O.S.
Calcium chromate

Apparatus: ICAP spectrophotometer
AA spectrophotometer with burner and graphite furnace

Analysis Method Parameters:

ICAP: Direct aspiration of sample solution
Analytical Wavelength - 267.7, 294.9 nm

AA: Analytical Wavelength - 357.9 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 1000°C - 30 sec
Atomize 2700°C - 10 sec
Argon purge gas
Background correction

Flame Conditions - Nitrous oxide - acetylene
Fuel rich

Detection Limits:

ICAP:	0.05 mg/L; 0.2-50 mg/L
Furnace AA:	1 µg/L; 5-100 µg/L
Flame AA:	0.05 mg/L; 0.5-10 mg/L

References:

1. U.S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," Report No. SW-846 (1980).

2. U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979).

Method Number:	A227
Method Name:	Lead
Basic Method:	Atomic spectroscopy
Matrix:	Solid and liquid wastes Solid effluents Scrubber water

Specific POHC/PIC from Appendix VIII to which method may be applied:

Lead
Lead compounds N.O.S.
Lead acetate
Lead phosphate
Lead subacetate
Tetraethyl lead

Apparatus:	ICAP spectrophotometer AA spectrophotometer with burner and graphite furnace

Analysis Method Parameters:

ICAP: Direct aspiration of sample solution
Analytical Wavelengths - 220.3, 217.0 nm

AA: Analytical Wavelength - 217.0 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 500°C - 30 sec
Atomize - 2700°C - 10 sec
Argon purge gas
Background correction

Flame Conditions - Acetylene - air
Oxidizing

Detection Limits:

ICAP:	0.1 mg/L; 1-100 mg/L
Furnace AA:	1 μg/L; 5-100 μg/L
Flame AA:	0.1 mg/L; 1-20 mg/L

Method Number: A229

Method Name: Nickel

Basic Method: Atomic spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber water

Specific POHC/PIC from Appendix VIII to which method may be applied:

Nickel
Nickel compounds N.O.S.
Nickel carbonyl

Apparatus: AA spectrophotometer with burner and graphite furnace
ICAP spectrophotometer

Analysis Method Parameters:

ICAP: Direct aspiration of sample solution
Analytical Wavelengths - 231.6, 227.0 nm

AA: Analytical Wavelength - 232.0 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 900°C - 30 sec
Atomize - 2700°C - 10 sec
Argon purge gas
Background correction

Flame Conditions - Air - acetylene
Oxidizing

Method Number: A231

Method Name: Selenium

Basic Method: Atomic spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber waters

Specific POHC/PIC from Appendix VIII to which method may be applied:

Selenium
Selenium compounds N.O.S.
Selenious acid
Selenium sulfide
Selenourea

Apparatus: AA spectrometer with graphite furnace
Hydride generator

Analysis Method Parameters:

AA: Analytical Wavelength - 196.0 nm

Hydride Generation:

Reduction with $SnCl_2$ or $NaBH_4$
Zinc metal added to drive off hydride
Flame - argon - hydrogen

Furnace Parameters - Dry 125°C - 30 sec
Ash 1200°C - 30 sec
Atomize 2700°C - 10 sec
Argon purge gas
Background correction

Detection Limits:

Hydride Generation - <1 µg/L; 2-20 µg/L
Furnace AA - 2 µg/L; 5-100 µg/L

Method Number: A232

Method Name: Silver

Basic Method: Atomic spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber waters

Specific POHC/PIC from Appendix VIII to which method may be applied:

Silver
Silver compounds N.O.S.

Apparatus: AA spectrometer with graphite furnace

Analysis Method Parameters:

ICAP: Direct aspiration of sample solution
Analytical Wavelength - 328.1, 224.6 nm

AA: Analytical Wavelength - 328.1 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 400°C - 30 sec
Atomize 2700°C - 10 sec
Argon purge
Background correction
Flame Conditions - Acetylene - air
Oxidizing

Detection Limits:

ICAP: 0.01 mg/L; 0.1-50 mg/L
Furnace AA: 0.2 μg/L; 1-25 μg/L
Flame AA: 0.01 mg/L; 0.1-4 mg/L

Method Number: A233

Method Name: Strontium

Basic Method: Atomic spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber waters

Specific POHC/PIC from Appendix VIII to which method may be applied:

Strontium sulfide

Apparatus: AA spectrometer with graphite furnace

Analysis Method Parameters:

ICAP: Analytical Wavelengths - 407.8, 346.4 nm

AA: Analytical Wavelength - 460.7 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 1000°C - 30 sec
Atomize 2500°C - 10 sec
Argon purge gas
Background correction

Flame Conditions - Nitrous oxide/acetylene flame
Fuel lean

Detection Limits:

ICAP: 2 μg/L; 0.05-10 mg/L
Furnace AA: .2 μg/L; .4→20 μg/L
Flame AA: .08 mg/L; .2→5 mg/L

References:

1. U.S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," Report No. SW-846 (1980).

2. U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979).

POHC/PIC ANALYSIS METHOD

Method Number: A234

Method Name: Thallium

Basic Method: Atomic Spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber waters

Specific POHC/PIC from Appendix VIII to which method may be applied:

Thallium
Thallium compound, NOS
Thallic oxide
Thallium(I)acetate
Thallium(I)carbonate
Thallium(I)chloride
Thallium(I)nitrate
Thallium selenite
Thallium(I)sulfate

Apparatus: AA spectrometer with graphite furnace

Analysis Method Parameters:

ICAP: Analytical Wavelengths - 190.9, 351.9 nm

AA: Analytical Wavelength - 276.8 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 400°C - 30 sec
Atomize 2400°C - 10 sec
Argon purge gas
Background correction
Flame Conditions - Air - acetylene
Oxidizing

Detection Limits:

ICAP:	0.1 mg/L; 1-100 mg/L
Furnace AA:	1 μg/L; 5-100 μg/L
Flame AA:	0.1 mg/L; 1-20 mg/L

References:

1. U.S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," Report No. SW-846 (1980).

2. U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979).

Method Number: A235

Method Name: Vanadium

Basic Method: Atomic spectroscopy

Matrix: Solid and liquid wastes
Solid effluents
Scrubber waters

Specific POHC/PIC from Appendix VIII to which method may be applied:

Vanadic acid, ammonium salt
Vanadium pentoxide

Apparatus: AA spectrometer with graphite furnace

Analysis Method Parameters:

ICAP: Analytical Wavelengths - 309.3, 214.0 nm

AA: Analytical Wavelengths - 318.4 nm

Furnace Parameters - Dry 125°C - 30 sec
Ash 1400°C - 30 sec
Atomize 2800°C - 15 sec
Argon purge gas
Background correction
Flame Conditions - Nitrous oxide - acetylene
Fuel rich

Detection Limits:

ICAP: 0.01 mg/L; 0.1-150 mg/L
Furnace AA: 4 μg/L; 10-200 μg/L
Flame AA: 0.2 mg/L; 2-100 mg/L

Digestion Procedure for Metals in Water

Transfer 250 mL of the well-mixed acid-preserved sample to a Griffin beaker. Add 3 mL of concentrated HNO_3. Place the beaker on a hot plate and evaporate to approximately 5 mL cautiously, making certain that the sample does not boil. Cool the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness (1 to 2 mL) and cool the beaker. Add 1.5 mL of concentrated HCl and 5 mL of deionized, distilled water and warm the beaker gently for 15 min to dissolve and precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized, distilled water, and filter the sample to remove insoluble material that could clog the nebulizer. Dilute to a final volume of 25 mL in a volumetric flask with deionized, distilled water. The sample is now ready for analysis. Aspirate the sample and calibration standards into the ICAP following the manufacturer's recommendations. Calibrate the instrument with calibration standards and set readout for direct output of concentration units. Analyze samples and the method blank (a distilled-water blank taken through the entire procedure above for the samples). Concentrations so determined shall be reported as "total."

Digestion Procedure for Metals in Soil

Weigh out 5.00 g of the dried soil sample into a 150-mL beaker. Add 10 mL of deionized, distilled water and 5.0 mL of concentrated nitric acid. Digest on a hot plate at 90 °C fir 3 h (do not boil). Filter into a 50-mL volumetric flask through White Ribbon 589 paper, with pulp, and wash and dilute to volume with deionized, distilled water. Shake well and remove a 5-mL aliquot, placing the aliquot in another 50-mL volumetric flask. Add 4.5 mL of concentrated nitric acid and dilute to the mark with deionized, distilled water. The sample is now ready for analysis. Aspirate the samples and calibration standards into the ICAP following the manufacturer's recommendations. Calibrate the instrument with calibration standards and set to readout for direct output of concentration units. Analyze samples and the method blank (a distilled-water blank taken through the above acid digestion).

The results obtained with the digestion and analysis procedure are presented in Tables D-2 and D-3. In general, the results obtained with spiked water samples were accurate and precise except for occasional high values obtained with the unspiked water samples. The results of the analysis of the soil samples were generally precise, but were biased by high responses to unspiked samples. Presumably the unspiked soil samples contained measurable quantities of the three metals. These blank responses were especially high for vanadium determinations. After correction for the average response to unspiked soil samples, the determinations of beryllium and strontium were generally acceptable, with recoveries ranging from 89 to 100%. The recoveries of vanadium calculated after correction for the blank responses were less accurate and ranged from 70 to 87%.

TABLE D-2. EVALUATION OF RECOMMENDED DIGESTION AND ANALYSIS PROCEDURES FOR BERYLLIUM, STRONTIUM, AND VANADIUM IN SPIKED WATER SAMPLES

Element	Test concn, µg/L	Observed concn for specified sample,[a] µg/L 1	2	3	4	Avg observed concn,[b] µg/L	RSD, %	Avg Recovery, %
Be	0.0	0.0	0.0	0.0	0.2	0.0	—	—
	5.0	4.8	4.9	4.8	4.8	4.8	1.0	96
	10.0	9.8	9.9	9.4	9.9	9.8	2.4	98
	20	20	20	19	20	20	2.5	100
	50	49	51	49	51	50	2.3	100
	100	99	100	95	100	99	2.4	99
Sr	0.0	1.2	0.1	0.1	3.0	1.1	—	—
	5.0	4.8	4.8	4.8	5.7	5.0	9.0	100
	10.0	9.6	9.7	9.6	11.0	10.0	6.9	100
	20	19	19	19	21	20	5.1	100
	50	48	50	50	51	50	2.5	100
	100	95	98	96	100	97	2.3	97
V	0.0	0.0	0.0	0.0	3.1	0.8	—	—
	5.0	5.3	4.7	4.4	5.8	5.1	12.4	102
	10.0	9.5	9.5	9.0	11.0	9.8	8.9	98
	20	19	20	19	21	20	4.8	100
	50	47	50	48	50	49	3.1	98
	100	93	98	95	99	96	2.9	96

[a] Results have not been corrected for responses to unspiked water samples.

[b] [(Avg observed concn)/(test concn)] x 100.

TABLE D-3. EVALUATION OF RECOMMENDED DIGESTION AND ANALYSIS PROCEDURES FOR BERYLLIUM, STRONTIUM, AND VANADIUM IN SPIKED SOIL SAMPLES

Element	Test concn, µg/L	Observed concn for specified sample,[a] µg/L				Avg observed concn,[b] µg/L	RSD, %	Avg recovery, %
		1	2	3	4			
Be	0.0	1.3	1.2	1.5	1.4	1.4	9.6	—
	5.0	5.9	5.8	6.0	5.9	5.9	1.4	90
	10.0	10.0	10.0	11.0	10.0	10.3	4.5	89
	20	20	20	20	20	20	0.0	93
	50	48	48	49	49	49	1.2	95
	100	96	95	97	95	96	1.0	95
Sr	0.0	13	13	13	14	13	3.8	—
	5.0	18	17	17	18	18	3.3	100
	10.0	22	22	22	24	22	4.4	90
	20	31	31	30	32	31	2.6	90
	50	60	60	62	61	61	1.6	96
	100	100	110	100	110	108	4.5	95
V	0.0	57	57	57	54	56	2.7	—
	5.0	61	62	59	58	60	3.0	80
	10.0	63	66	63	64	64	2.2	80
	20	70	72	69	68	70	2.4	70
	50	99	100	93	98	98	3.2	83
	100	140	150	140	140	143	3.5	87

[a] Results have not been corrected for responses to unspiked soil samples.

[b] [(Avg observed concn)/(test concn)] x 100. This value has been corrected for the responses to the unspiked soil samples.